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The Interpretation of Phase Equilibrium Diagrams

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PHASE equilibrium diagrams representing the relation between composition and temperature with reference to the melting and crystallizing processes in mixtures containing several components offer a means of expressing in compact and graphic form a large amount of information of a type which is fundamental to the comprehension of many factors vital to ceramic engineering and glass technology. To those conversant with such diagrams the information thus available is apparent at a glance, but a considerable amount of thought and study and actual use of these diagrams is necessary to attain such a degree of competence. It is the purpose of this paper to explain the use of phase equilibrium diagrams in as simple a manner as possible, using as illustrations diagrams fundamental to the glass industry.

Much of the subsequent discussion is based on purely geometrical relationships, and it is pertinent to inquire into the reason for this intimate connection between geometry and chemistry. It arises in part in the methods used in expressing composition by means of geometrical figures; but in larger part in the thermodynamic relationships underlying the study of heterogeneous equilibrium. The entire structure on which is based the study of heterogeneous equilibrium is due to the genius of J. Willard Gibbs, and is developed in detail in his "Equilibrium of Heterogeneous Substances."[1] In this paper the application of the first and second laws of thermodynamics is extended to substances containing independently variable components, in contrast to the previous restriction to substances of invariable composition. One consequence of that treatment is the Phase Rule, as it is usually called. In its usual form this is but an incidental qualitative consequence of equations which express the relationship between those quantities which connect the thermodynamic stability of the different phases with their composition. These equations may be applied either analytically, or, as is commonly done, graphically. Gibbs himself showed how to make a graphic representation of the stability relationships of phases of both fixed and variable composition, by means of curves and surfaces, and, indeed, the use of the equilateral triangle for representing composition in three-component systems is due to Gibbs. As will be seen later, a triangular phase equilibrium diagram representing a three-component system is divided into various fields or regions by boundary curves, and these boundary curves represent the projection on to the basal plane of curves representing the limits of thermodynamic stability, as expressed by the fundamental equations of the various phases. It is from a consideration of the fundamental equations, or of the surfaces of thermodynamic stability derived from them, that the various theorems are derived which govern our application of geometric laws to the chemical relationships expressed in phase equilibrium diagrams.

The first system to be discussed is that formed by sodium metasilicate and silica,[2] shown in Fig. 1. The vertical scale represents temperature, the horizontal scale, composition. This is part of the larger system, Na_2O-SiO_2, and the composition is given in per cent of SiO_2 by weight, considering Na_2O as the other component. The designation of the components in such a case is largely a matter of convenience. $Na_2O.SiO_2$ and SiO_2 could as well have been chosen as components, as was done by Morey and Bowen in their original paper, and the phase relationships are equally well shown by such a choice. Also, the composition could have been expressed in molecular per cent, using either Na_2O or $Na_2O.SiO_2$ as components, and that again is a matter of convenience. Since Na_2O and SiO_2 have molecular weights so nearly equal, their relation as components would give a

[1] "The Scientific Papers of J. Willard Gibbs," vol. 1, p. 55. Longmans, Green & Co.

[2] G. W. Morey and N. L. Bowen, J. Phys. Chem., 28, 1169 (1924). F. C. Kracek, J. Phys. Chem., 34, 1583 (1930).

diagram almost identical with that obtained by the form of representation used in Fig. 1; but if mol per cent were used with $Na_2O.SiO_2$ and SiO_2 as components the resulting diagram would, because of the high molecular weight of $Na_2O.SiO_2$, have appeared distorted. Whatever the choice of components, however, the point representing a given composition is the center of gravity when the quantities of the two components corresponding to that composition are placed at the ends of the axis of abscissa. This question of representation by mol per cent and weight per cent will be reverted to subsequently.

Since this is a system of two components, at constant pressure, coexistence of three phases gives an invariant system; two phases, a monovariant system; and if only one phase is present the system is divariant. The region in Fig. 1 inscribed "liquid," above the various freezing point curves, represents a divariant system and neither composition nor temperature is fixed by any of the properties under consideration. At a temperature above the liquid and solid surface a whole series of unsaturated liquids may exist, and a given composition may be liquid over a wide range of temperatures. But when a liquid cools to the temperature represented by a freezing point curve, another phase makes its appearance, and the system loses one degree of freedom. If a liquid containing 80% SiO_2 is cooled, at about 1135° crystals of tridymite, the form of crystalline SiO_2 stable from 870 to 1470°, separate, and this temperature is uniquely determined by fixing the composition. Only one liquid can coexist with tridymite at 1135°. If a mixture of tridymite and glass, of a gross composition richer in Na_2O than 20 per cent, is held at 1135°, the crystals will all dissolve, and the point in the diagram representing that composition at that temperature will be in the divariant field of liquid alone. If the gross composition of the mixture is richer in SiO_2 than 80%, but contains a larger proportion of crystals than corresponds to equilibrium, tridymite will dissolve until the liquid has exactly the composition 20% Na_2O, 80% SiO_2. The point representing this composition lies within the field "Tridymite-liquid," every point of which represents a mixture of these two phases. The composition of the solid phase is constant, that of the liquid changes as shown by the freezing point curve; and the relative proportions of the two phases in any mixture represented by a point in this field are given by the inverse ratio of the length of the portions into which this point divides the horizontal distance from the liquidus to the SiO_2 side of the figure. For example, if the temperature is such that the liquid contains 78% SiO_2, and the gross composition of the mixture is 80% SiO_2, it will consist of 20 parts of liquid and 2 parts of tridymite; while if the gross composition is 98% SiO_2 the proportions will be 2 parts of liquid, of the same composition as before, and 20 parts of tridymite.

Corresponding to every liquid composition there is a temperature at which it can coexist in equilibrium with crys-

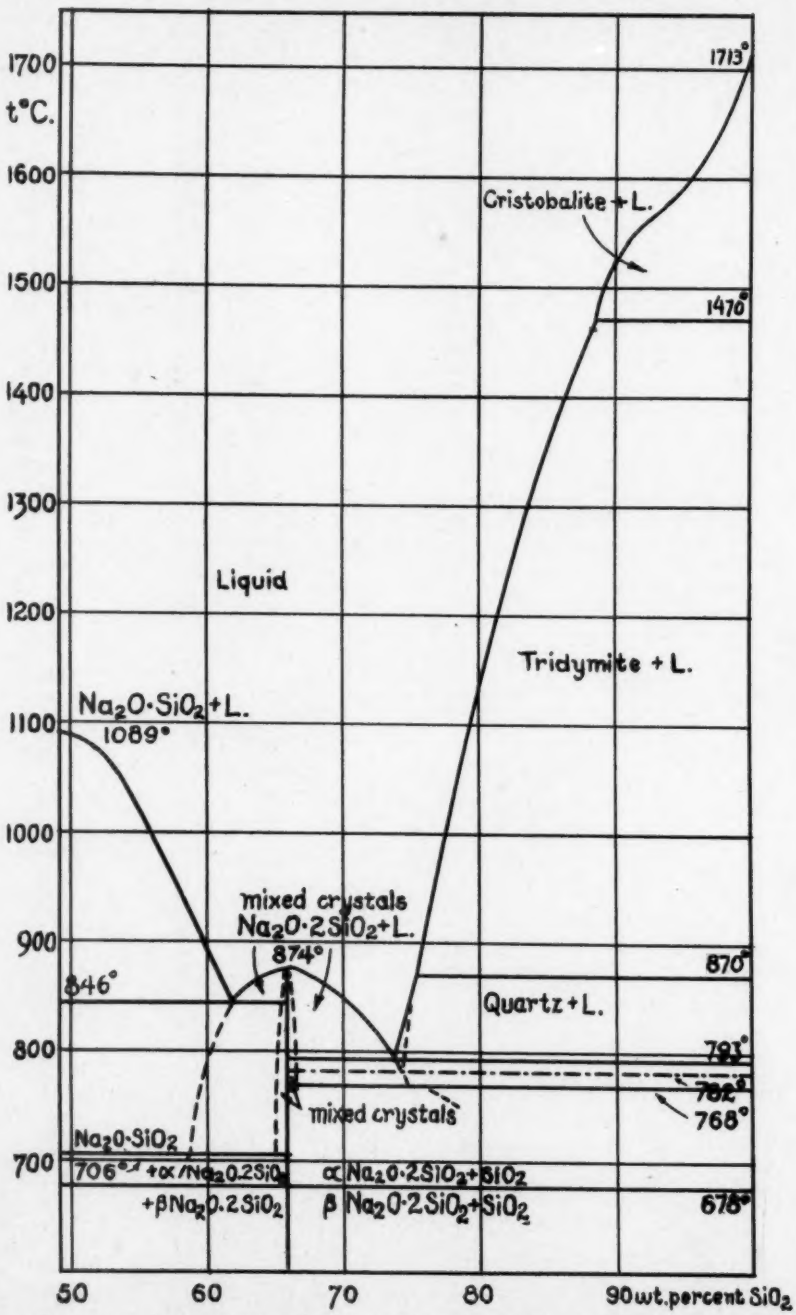

FIG. 1. PHASE EQUILIBRIUM DIAGRAM OF THE BINARY SYSTEM, Na_2SiO_3-SiO_2.

tals, and that temperature is called the liquidus temperature. The liquidus curve of a given compound is an example of a monovariant system, because fixing either one of the variables, temperature or composition, fixes the other. The intersection of two such monovariant curves results in the coexistence of three phases, two solid and one liquid. Such a system is invariant, hence both temperature and liquid composition are fixed. Three types of invariant points found in this system will be considered in detail. One of these is illustrated by the intersection of the quartz liquidus and the tridymite liquidus, at 870°. Here the invariant point is a maximum temperature for one of the crystalline phases, quartz; a minimum temperature for the other, tridymite; and liquid is stable both above and below the invariant point. The chemical composition of the two solid phases is the same, and this type of invariant point is called an inversion point; if there is no solid solution, as is true in this case, the temperature is independent of the presence of the liquid phase, or of the complexity of that liquid. Of similar type are the tridymite-cristobalite inversion at 1470°, and the α-β inversion of $Na_2O.2SiO_2$ at 678°, shown in Fig. 1.

Another type of invariant point is illustrated by the intersection of the quartz and the sodium disilicate melting point curves. This intersection takes place at 793° and a liquid composition of 73.9% SiO_2. Here the liquid is intermediate in composition between the two solid phases, and whenever the liquid phase can be made up by mixing the two coexisting solid phases the invariant point is a point of minimum temperature for liquid, and is called a eutectic. The metastable $Na_2O.2SiO_2$-tridymite eutectic shown in Fig. 1 at 782°, 74.6% SiO_2 is an example of a phase persisting under conditions in which it is unstable, a phenomenon frequently met with in silicate systems, but not uncommonly occurring with more reactive substances. Another eutectic is that between $Na_2O.SiO_2$ and $Na_2O.2SiO_2$ at 846° and 62.1% SiO_2.

Since a eutectic is a minimum temperature for liquid, at such a point all liquids freeze completely. A liquid containing 50% SiO_2 will begin to freeze at 1088°, and as cooling continues, and $Na_2O.SiO_2$ continues to separate, the composition of the liquid will follow the freezing point curve of sodium metasilicate, until the eutectic is reached. At an intermediate temperature any mixture in the field "$Na_2O.SiO_2$-L" will be either all liquid, if the temperature is above the liquidus for the composition in question, or a mixture of liquid and $Na_2O.SiO_2$ crystals, if below the liquidus. For example, a mixture containing 58% SiO_2 will be all liquid above 955°; at 955° it will begin to crystallize; at 900° it will be a mixture of (60-58) parts $Na_2O.SiO_2$ crystals, (58-49.21)[3] parts liquid. When the eutectic is reached it will be a mixture of (62.1-58) parts $Na_2O.2SiO_2$ and (58-49.21) parts eutectic liquid. Then $Na_2O.2SiO_2$ crystallizes out at constant temperature, and the mixture solidifies completely to a mixture of (65.96-58) parts $Na_2O.SiO_2$ and (58-49.21) parts $Na_2O.2SiO_2$.

There are two congruent melting points, of the compounds $Na_2O.SiO_2$, at 1089°, and $Na_2O.2SiO_2$, at 874°. These may be considered as fixed points in a one-component system; but they are better considered as two-component invariant points, in which the necessary number of equations to completely determine all the variables are given by the fundamental equations of the two coexisting phases, liquid and crystalline, and the additional equation expressing the equivalence of composition of these two phases.

The preceding discussion has assumed that equilbrium is reached in all the phase reactions; and in the study which established the diagrams every precaution was taken to insure that equilibrium was reached. The persistence of a liquid phase to temperatures below which it is stable, known as undercooling, is not peculiar to glasses, or even to silicates. In considering the properties of glasses or glass-forming systems, it is well to bear in mind that the chemistry of silicates differs not in kind but only in degree from that of the more usual compounds. Those particular compositions of matter which have been hit on for glasses have the common characteristic that they exhibit a great reluctance to pass from the liquid to the crystalline condition even under the most favorable circumstances, a characteristic possessed in a less or even a greater degree by many substances wholly unsuitable for use as glass. Many organic substances fall in this category, of which glucose solutions may be taken as an example. Some complex sulphate solutions may be obtained in a glassy form; As_2O_3 and Sb_2O_3 can both be obtained as glass, as can some of their compounds; phosphates are well-known as glass formers, and indeed, the so-called meta- and pyro-phosphoric acids probably are only known in the glassy condition; and the oxide B_2O_3 has never yet been obtained in the crystalline condition. Some entirely silicate-free glasses have been articles of commerce. Among silicates, glasses of the composition of the minerals albite and orthoclase are far more resistant toward crystallization than any commercial glasses. The phenomenon of undercooling is a usual observation with molten salts, and the glasses of commerce represent mixtures in which not only is this property of undercooling to form glasses strongly marked, but in addition the resulting glasses possess other properties which make them useful.

The methods which were used in studying the phase equilibrium relationships in the sodium silicate system are characteristic of those used in all such studies and are different from those commonly used. With salts and metals, the phase transformations may be followed by means of heating or cooling curves. When such materials are heated at a uniform rate, an absorption of heat takes place when melting begins, which is indicated by the temperature of the charge falling behind that of the furnace, or even remaining constant. Because of the slowness of the melting process in devitrified glasses, as well as in many other silicate melts, no indication of the beginning of melting can be found on the heating curve; and, indeed, the material may even be superheated many degrees above the temperature of melting without much formation of liquid. This condition is, of course, unstable and, if held above the requisite temperature, the crystals will dissolve, but overheating is the common occurrence. Similarly, on cooling the glass does not freeze—that is why it remains a glass—and hence the type of discontinuity which gives so marked an effect in the freezing of a metal cannot be observed. If held long enough, how-

[3] The liquid phase at 900° contains 60% SiO_2 and the compound $Na_2O.SiO_2$, 49.21% SiO_2.

ever, crystals will separate. Accordingly the "quenching" method is used in studying such mixtures. A few milligrams of the material, wrapped in thin platinum or gold foil, are held at a known constant temperature long enough for equilibrium to be reached, which may be a matter of hours, days, or even weeks. Then the charge is cooled in such a manner as to freeze the equilibrium, and examined with the petrographic microscope; if all glass, the temperature of heat treatment was above the liquidus; if a mixture of glass and crystals, it was below the liquidus. By measuring the properties of the crystals they can be positively identified. With difficult mixtures it is customary to have two charges side by side, one initially glass, the other previously crystallized. The heating must be continued long enough for both charges to attain the same condition.

With the exception of compositions near to the disilicate-quartz eutectic there is little difficulty in reaching equilibrium in the $Na_2O.SiO_2$-SiO_2 system by maintaining the charge at constant temperature, and over most of the composition range an excessive time is not required. At the same time, it should be emphasized that crystallization processes, even though well under way, are quickly checked by slow cooling, and it is easy to obtain any desired intermediate stage. Sodium metasilicate can be studied either by the quenching or the heating curve method. It crystallizes so readily that large melts cannot be cooled as glass, but always crystallize. On the other hand, it undercools to such an extent that the cooling curve method is not reliable. Sodium disilicate is not difficult to crystallize, at least not in comparison with many commercial glasses; yet thousands of tons of glass of that composition had been made without obtaining the compound until the work of Morey and Bowen. Special attention should be called to the $Na_2O.2SiO_2$-quartz eutectic. There is here a remarkable melting point lowering; addition of 25% Na_2O lowers the melting point from 1710° to 793°, almost 1000°. The low temperature of this eutectic has important implications in geology, and is of the first importance to glass technology. Glass of this composition would indeed be excellent were it not for the fact that it is easily attacked by water, and hence is not stable in the air. It is, of course, essential that glass be stable on exposure not only to the air but also to far more drastic treatment, and for this reason other oxides must be added to stabilize this eutectic. Nevertheless, about a half million tons of sodium silicate glass of essentially this composition is manufactured annually for use in the soluble silicate industry, and devitrification troubles are unknown. To crystallize mixtures near this eutectic it is necessary to hold the charge just below the eutectic temperature for a long time, and the last stages of the devitrification take place even more slowly than the initial formation of crystals, showing that equilibrium is difficult to secure.

The ternary system, $Na_2O.SiO_2$-$CaO.SiO_2$-SiO_2, will next be considered. Details of this system are given in Figs. 2, 3, 4, 5, and 6. Figs. 2 and 3 are parts of the larger equilateral triangle whose vertices represent pure Na_2O, CaO and SiO_2. In such an equilateral triangle, the point representing a desired composition is the center of gravity of the triangle when loaded at each corner with the proportional quantities of that component. A point on a side represents a mixture containing only two components, the one represented by the opposite apex being absent; the points on a line through any apex represent mixtures in which the ratio of the other components remains constant; and the points on a line parallel to a side represent mixtures in which the percentage of the component represented by the apex opposite to that side is constant. For example, points on the side, Na_2O-SiO_2, represent the same binary system shown in Fig. 1; points on a line through SiO_2 and the compound, $Na_2O.2CaO.3SiO_2$, represent mixtures in which the Na_2O:CaO ratio is 1:2; and all mixtures lying on a line parallel to the Na_2O-SiO_2 side have the same CaO content. In the figure the scale is indicated on the sides, and may be transferred into the interior of the diagram by coordinate lines parallel to the sides. This method of representing composition in a system of three components has the advantage of symmetry, and is more convenient except when one component is present in preponderant amount, as is frequently the case with water and salt systems. Other methods which can be used are discussed in detail by Roozeboom.[4] In Fig. 5, right-angled coordinates are used, in which the weight per cent SiO_2 is indicated along the horizontal axis, weight per cent CaO along the vertical axis, and the weight per cent Na_2O obtained by subtracting from 100 the sum of CaO and SiO_2. This diagram represents the same composition range as that included within the broken lines of Fig. 3, and may be regarded as derived from the rhombus of that figure by means of a shear. The entire diagram of Fig. 3 can be similarly represented by opening out the angle opposite the CaO-SiO_2 side from 60° to 90°, and Fig. 6 shows the resulting distorted diagram.

Changing the method of representation from weight per cent to mol per cent also produces a distortion, in amount depending on the differences in the molecular weights of the various components. Either type of diagram can be obtained from the other by the appropriate extension or compression of the different axes, but it is important to remember that in any such distortion straight lines remain straight lines. A mixture of $CaO.SiO_2$ and $Na_2O.2SiO_2$ remains on the straight line joining these two compounds no matter whether an equilateral or a right-angled triangle is used, or whether the oxides of any desired binary or ternary compounds are chosen as components, or whether composition is expressed in weight or mol per cent of those oxides or components. That being so, it is evident that much of the discussion in regard to the advisability of planning experiments on the variation of properties with composition by replacing a given oxide by another, for example, Na_2O by CaO, in molecular equivalent amounts, or per cent for per cent, which amounts to keeping the ratio of the other two oxides constant, in a three-component system, or by simply adding the oxide in question to the parent glass, is pointless. In any case the variation in composition is on a straight line in the composition diagram. If the original glass, for example, is a sodium silicate glass, with the Na_2O:SiO_2 ratio equal to 1:3, hence containing 74.4% SiO_2, on replacing Na_2O by CaO in molecular equivalent amounts the mixtures will lie on the straight line along which the ratio (Na_2O+CaO):

[4] H. W. Bakhuis Roozeboom, Die heterogenen Gleichgewichte, Friedr. Vieweg & Sohn, Braunschweig, 1911, Heft 3, Teil 1.

SiO_2 is 1:3, which extends from 74.4% SiO_2 on the Na_2O-SiO_2 side to 76.3% SiO_2 on the CaO-SiO_2 side. If the replacement is by weight per cent the straight line is that of constant SiO_2. If CaO is added to the orginal glass the composition will change along a straight line from the original sodium silicate glass to the CaO apex of the component triangle. All of these types of variations, and any similar ones that may be devised, will be represented by straight lines by all such methods of representation if they are straight in one of them. It may be well to remark, in connection with such linear excursions into ternary or more complicated systems as have been discussed above, that any deductions concerning the variation of properties with composition made on the basis of such excursions must be accepted with caution. It is not possible to make sweeping generalizations as to the effect of the replacing of Na_2O by CaO on the basis of such a linear excursion into the ternary diagram. Replacing Na_2O by CaO in a trisilicate glass raises the melting point, but from that it does not follow that some other variation will not lower the melting point, and we can see from Fig. 2 that there is a large composition area in which the melting point is lower than that of a $Na_2O.3SiO_2$ glass.

The case is similar with regard to such properties as density and refractive index. The lines of constant density in the triangular composition diagram are curves, whose curvature changes along each curve, and differs in different parts of the diagram, and no linear variation in composition can give an insight into the general relationships. It happens that the curvature is slight in the region of commercial glass composition, and if the experimental work is not too well done it can be represented by additive functions within the error of measurement. No generalizations in regard to the system as a whole are justified by the circumstance that the variation of some property along some arbitrary straight line

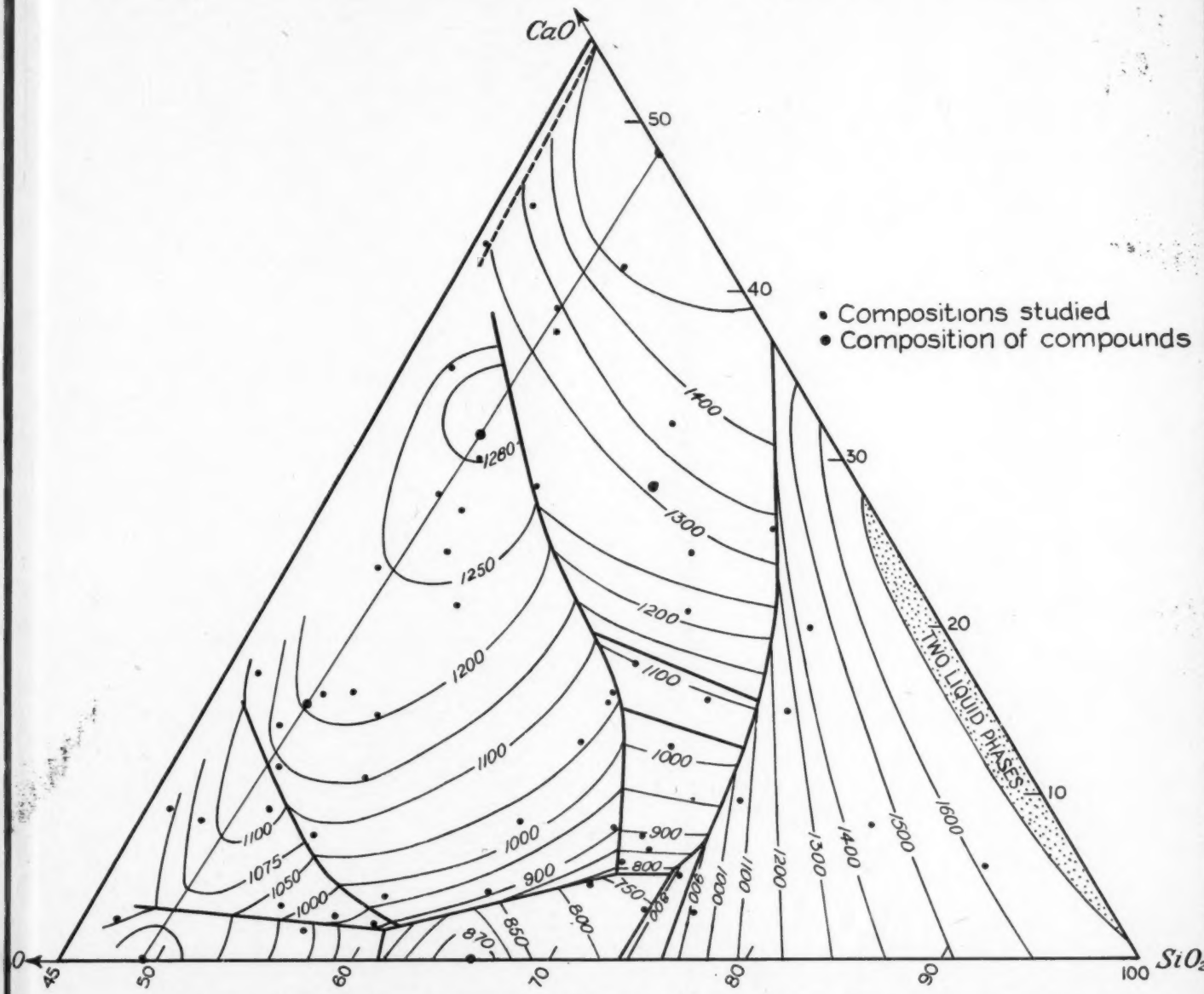

FIG. 2. PHASE EQUILIBRIUM DIAGRAM OF THE TERNARY SYSTEM, $Na_2O.SiO_2$-$CaO.SiO_2$-SiO_2, SHOWING ISOTHERMS.

shows a maximum, a minimum, or neither. Neither is there any virtue in expressing the variation with composition of the physical properties of glass in terms of the percentages of various compounds, even though such compounds may exist in the solid state. One of the characteristics of silicate melts in general, and of those compositions which are used for glass in particular, is that the compounds which separate on crystallization are largely dissociated in the liquid state. The type of dissociation referred to is not an electrolytic dissociation similar to that met with in aqueous solutions, but one more allied to gaseous dissociation, in which molecular complexes suffer rearrangement, and the condition of a glass at a temperature at which its molecules are free to rearrange themselves will probably correspond to transitory groupings containing representatives of all the possible molecular arrangements of the components, the relative amounts of the different grouping at any one time being determined by the temperature according to the usual thermodynamic laws. It may be that some distortion of the diagram will tend to rectify some curved lines, or at least diminish their curvature, but it will be found that none of the properties of glass are truly additive, and a distortion which produces the desired effect in one part of the diagram may make matters worse in another part.

The complete representation of the three composition variables in a plane is made possible by the additional restriction that their sum be 100 per cent, thus reducing the independent variables to two. Temperature must be expressed in a third dimension, and is represented by the vertical distance from the base. The equilateral prism thus obtained is terminated by a complex upper surface, representing the liquidus temperatures in the various fields, and a

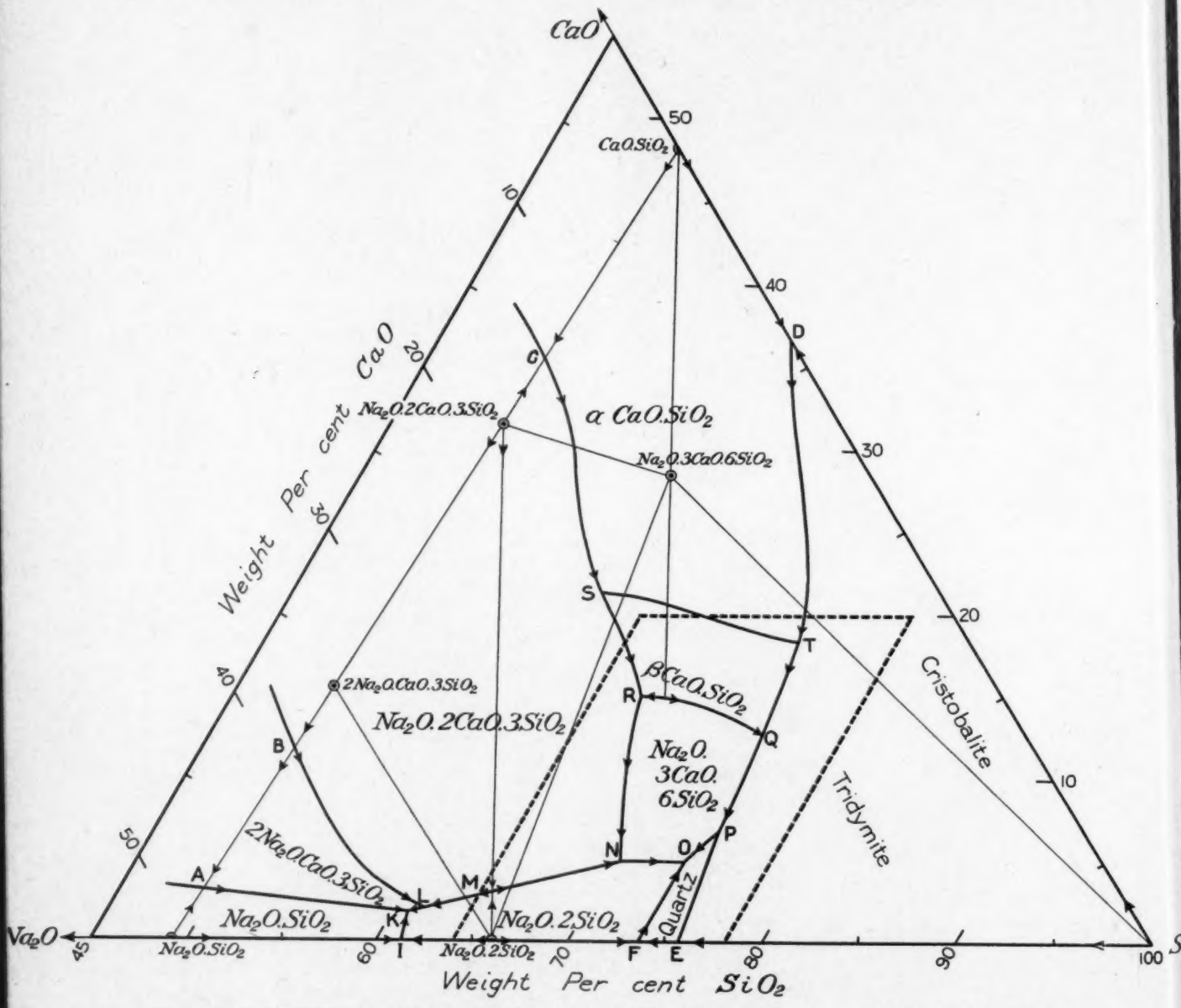

FIG. 3. SKETCH SHOWING THE BOUNDARY CURVES AND TIE-LINES IN THE TERNARY SYSTEM, $Na_2O.SiO_2$-$CaO.SiO_2$-SiO_2.

photograph of such a model is shown in Fig. 4. If planes parallel to the base be passed through this model at appropriate heights they will intersect the surfaces in curved lines, giving the composition of the liquids which can coexist with the solid at that temperature, and the isotherms shown in Fig. 2 may be regarded as the projection of such intersections onto the basal plane.

Consider now the ternary diagrams, preferably Fig. 3. It is divided by heavy curved lines, the projections of the

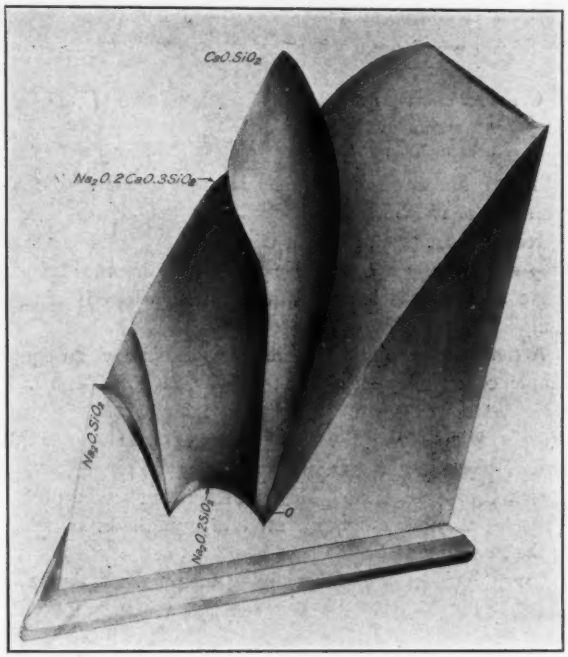

FIG. 4. SKETCH OF SOLID TEMPERATURE-COMPOSITION MODEL OF THE TERNARY SYSTEM, $Na_2O.SiO_2$-$CaO.SiO_2$-SiO_2.

valleys between the various mountain slopes of Fig. 6, into several fields, and the direction of falling temperature along these boundaries is indicated by arrows. Within each of the fields a different substance is the first to crystallize on cooling, or the last to dissolve on heating. For example, from all mixtures whose compositions lie within the area BCSRNML, the compound $Na_2O.2CaO.3SiO_2$ is the primary phase, and this area is called the field of $Na_2O.2CaO.3SiO_2$. As the liquid is cooled, and more and more of this compound separates, the composition of the residual liquid changes, and, since the crystals and the residual liquid are being formed out of the original liquid, all three compositions must lie on a straight line, with the composition of the original liquid between the other two, and dividing the line into segments inversely proportional to the relative amounts of the two phases. This is, of course, the same type of relationship that has already been discussed, with the aid of numerical examples, in the binary system.

As crystallization continues, the composition of the liquid will be continuously displaced on a straight line radiating out from the composition of $Na_2O.2CaO.3SiO_2$, until that line intersects one of the boundary curves, and the system becomes monovariant. With three components at constant pressure, coexistence of two phases produces a divariant system, illustrated by the field of any compound. Divariance in this case means that at any temperature a large number of different liquids may coexist with the solid phase, and that fixing the temperature does not automatically fix the composition of the liquid. When the system becomes monovariant by the appearance of a second crystalline phase the composition of the liquid becomes fixed when the temperature is fixed, and at any given temperature only one liquid composition can coexist with the two crystalline phases.

If the original liquid can be made up of the two crystalline phases that separate at the boundary curve, for example if it lies on the line joining $Na_2O.2SiO_2$ with $Na_2O.2CaO.3SiO_2$, at point M, then it will freeze entirely at this point, and the mixture may be regarded as a binary system within the ternary system because every reaction that takes place can be expressed in terms of the two end members alone. It is important to see this distinction between those pairs of compounds which form truly binary systems, and those which do not. $Na_2O.2SiO_2$ and $CaO.SiO_2$ do not form a binary system. When $CaO.SiO_2$ is added to $Na_2O.2SiO_2$, the resulting compositions will follow the straight line joining these two compounds, and the phase changes which will take place can be foretold from the fields which this tie-line crosses. The liquidus temperature will first fall, while the point remains within the field of $Na_2O.2SiO_2$; but it will be seen that when a boundary is reached it is that of $Na_2O.2CaO.3SiO_2$. This compound does not lie on the tie-line in question; separation of a compound less silicic than corresponds to the tie-line must of necessity leave a liquid more silicic, and it is evident that the behavior of mixtures of these two compounds, $Na_2O.2SiO_2$ and $CaO.SiO_2$, cannot be expressed without reference to the ternary system.

It will be observed that the composition of the compound, $Na_2O.2CaO.3SiO_2$, lies within the field of this compound; a liquid of this composition will freeze completely to this compound when cooled, and when the compound is heated it shows a sharp melting point. Such a melting is called congruent. Within the same field is shown the composition of another compound, $2Na_2O.CaO.3SiO_2$, but the field of this compound is represented by the area ABLK. Only from mixtures within this field does $2Na_2O.CaO.3SiO_2$ crystallize as primary phase. When the pure crystalline compound is heated it remains unchanged until the temperature of the point B is reached. Then it begins to decompose into a liquid of the composition B, and $Na_2O.2CaO.3SiO_2$, and above the temperature, and at the liquidus, the latter compound is the crystalline phase coexisting with liquid. Such a melting is called incongruent, and the phenomena taking place at this point are entirely analogous to those which take place at the transition point of a salt hydrate. When $Na_2SO_4.10H_2O$ is heated, at its transition point it decomposes into anhydrous Na_2SO_4 and saturated solution. In the binary system, H_2O-Na_2SO_4, this is an invariant point, and indeed it is a fixed point whose equilibrium temperature is known to a high degree of accuracy. But if excess of either H_2SO_4 or NaOH be present, the temperature is no longer fixed, but is monovariant; the transition temperature of the hydrate will be lowered in either acid or alkaline

solutions. The case is exactly analogous in the silicate system. Point B is an invariant point in the binary system, $Na_2O.SiO_2$-$CaO.SiO_2$, but is only one point on the curve BL, the monovariant equilibrium $2Na_2O.CaO.3SiO_2$-$Na_2O.2CaO.3SiO_2$-liquid. It is, however, a point of maximum temperature along this curve.

Mixtures of the two compounds, $Na_2O.SiO_2$ and $CaO.SiO_2$, form a binary system, because the two fields crossed, those of $2Na_2O.CaO.3SiO_2$ and $Na_2O.2CaO.3SiO_2$, may be regarded as compounds between the two end members. Addition of $CaO.SiO_2$ to $Na_2O.SiO_2$ lowers the melting point of the latter, until the binary eutectic is reached at A. On further addition of $CaO.SiO_2$, the melting point curve rises, with $2Na_2O.CaO.3SiO_2$ as solid phase, until the incongruent melting point of this compound is reached, at B. This is an invariant point in the binary system, and the temperature remains constant until all $2Na_2O.CaO.3SiO_2$ is decomposed, and the only crystals left are those of $Na_2O.2CaO.3SiO_2$. Addition of excess of any of the components, however, brings us into the ternary system, in which coexistence of these three phases produces, not an invariant, but a monovariant system, and the temperature falls in each direction from B. On further addition of $CaO.SiO_2$, the melting point continues to rise to the congruent melting of $Na_2O.2CaO.3SiO_2$, then falls to the eutectic between this compound and $CaO.SiO_2$, then rises to the melting point of $CaO.SiO_2$.

Of the two ternary compounds already considered, one has an incongruent, the other a congruent, melting point. But the one with a congruent melting point undergoes unusual dissociation in the liquid phase, as is shown by the shape of its melting point curve. A third ternary compound is met with in this system, of the composition, $Na_2O.3CaO.6SiO_2$, and it is an extreme case of a compound with an incongruent melting point. The pure compound decomposes at 1,060° into liquid and crystals of $CaO.SiO_2$, and the melt does not become entirely liquid until 1325°. This compound is characterized by an extreme reluctance to crystallize, and every composition in which it is primary phase is a practical glass composition on a manufacturing scale. Its field is shown in Figs. 3 and 4 by the area NOPQR, and on a larger scale in Fig. 5, which includes only compositions from 64 to 78% SiO_2, 0-20% CaO, by weight.

The other fields in the diagrams require little discussion. The three forms of crystalline silica, cristobalite, tridymite and quartz, occupy fields the limits of which, as long as the boundaries are between forms of silica, are determined solely by the temperature. The region of immiscibility need not concern us here. The two sodium silicates occupy fields which run down to either one or the other of the ternary eutectics. $CaO.SiO_2$ appears in two crystalline forms: α-$CaO.SiO_2$, or pseudo-wollastonite, the high temperature form, and β-$CaO.SiO_2$, the low temperature form, identical with the natural mineral, wollastonite. The boundary between these forms is the line ST, and as far as our information goes at present there is no solid solution in either form, and hence the temperature is constant along this curve. An investigation of this question is at present under way, but it is hampered by the sluggishness with which the inversion from the high temperature form to the low temperature form takes place. The high temperature form frequently separates in the stability field of the low form, and, indeed, in the upper part of this field it is the more common. Also, both forms frequently occur together at lower temperature, and once formed, the change from pseudo-wollastonite to wollastonite takes place very slowly indeed.

The sequence of phase and composition changes beginning with the first formation of crystals at the liquidus, to the final complete solidification to a conglomerate of crystalline phases is called a crystallization path. Crystallization paths afford a clear insight into the meaning of phase equilibrium diagrams, and a number of typical ones will be discussed in detail.

Consider first a mixture in the area $Na_2O.SiO_2$-AKI. Any composition within the area deposits $Na_2O.SiO_2$ as primary phase; the liquid follows a crystallization path lying on the straight line joining the liquid composition with that of $Na_2O.SiO_2$, until either the boundary AK or IK is reached. Here, either $2Na_2O.CaO.3SiO_2$ or $Na_2O.2SiO_2$, respectively, appears, and the liquid follows the boundary curve down to the ternary eutectic at K, where it solidifies completely.

A composition within the area, ABLK, follows an equally simple course, depositing first $2Na_2O.CaO.3SiO_2$, then, in all cases except those compositions lying within the small area between L and the line joining K with $2Na_2O.CaO.3SiO_2$, depositing $Na_2O.SiO_2$ as secondary phase. Within the small area mentioned, $Na_2O.2SiO_2$ is the second phase to separate; in both cases, the mixture crystallizes completely at the ternary eutectic K.

Crystallization of mixtures lying within the region where $Na_2O.2CaO.3SiO_2$ is the primary phase is usually a less simple matter. Consider first a composition within the triangle, $Na_2O.SiO_2$-$Na_2O.2SiO_2$-$2Na_2O.CaO.3SiO_2$, bounded by the curve, BL, and the straight line joining L with $Na_2O.2CaO.3SiO_2$. The primary phase is $Na_2O.2CaO.3SiO_2$; the liquid follows a crystallization path passing through the composition of the primary phase and of the original mixture, until this path cuts the boundary curve BL. At this intersection $2Na_2O.CaO.3SiO_2$ crystallizes; the liquid then follows the boundary curve, the reaction, $Na_2O.2CaO.3SiO_2$ + liquid = $2Na_2O.CaO.3SiO_2$, takes place, and the proportion of the former compound decreases, while that of the latter increases, until at L, where $Na_2O.2SiO_2$ appears, the compound, $Na_2O.2CaO.3SiO_2$, has been decomposed entirely. The liquid then follows the boundary curve, LK, finally solidifying completely at the ternary eutectic, K, to a mixture of $Na_2O.SiO_2$, $Na_2O.2SiO_2$, and $2Na_2O.CaO.3SiO_2$. If the composition lies within the same triangle, but to the right of the join, L—$Na_2O.2CaO.3SiO_2$, the end products will be the same, but the secondary phase will be $Na_2O.2SiO_2$, on the boundary ML; at L, reaction takes place resulting in the formation of $2Na_2O.CaO.3SiO_2$ and the disappearance of $Na_2O.2CaO.3SiO_2$.

Any mixture in the triangle, $Na_2O.2CaO.3SiO_2$-$2Na_2O.CaO.3SiO_2$-$Na_2O.2SiO_2$, will solidify completely to a mixture of the above phases and $Na_2O.2SiO_2$, but the crystallization path will differ according to the side of the line, L-$Na_2O.2CaO.3SiO_2$, on which the original composition lies. If the point representing the composition of the glass

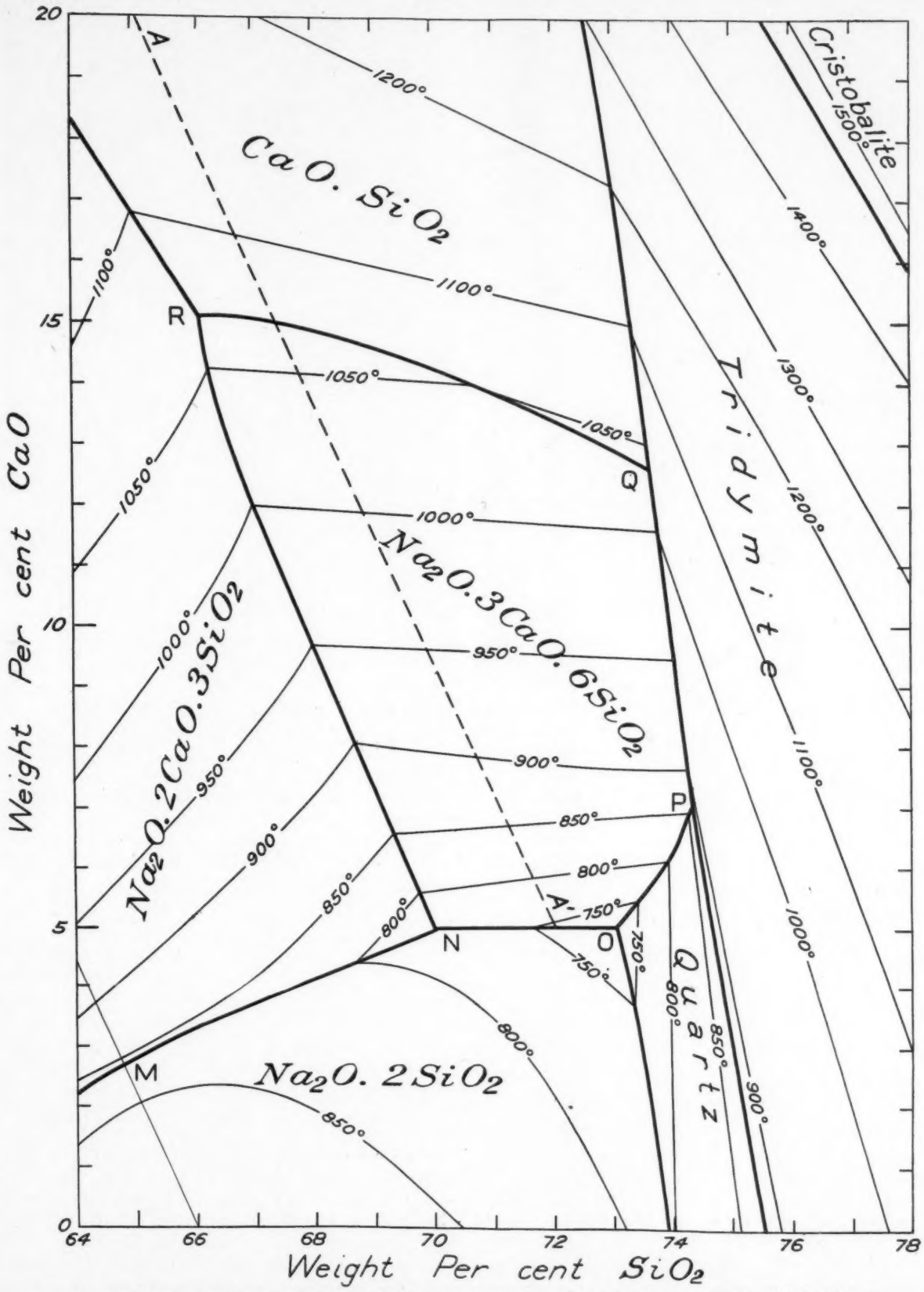

FIG. 5 THE ISOTHERMS AND BOUNDARY LINES IN THAT PORTION OF THE TERNARY SYSTEM, $Na_2O.CaO.SiO_2$, OF INTEREST IN GLASS TECHNOLOGY. WEIGHT % SiO_2 IS INDICATED ALONG THE HORIZONTAL AXIS; WEIGHT % CaO ALONG THE VERTICAL AXIS; WEIGHT % Na_2O IS OBTAINED BY SUBTRACTING THE SUM OF CaO AND SiO_2 FROM 100%.

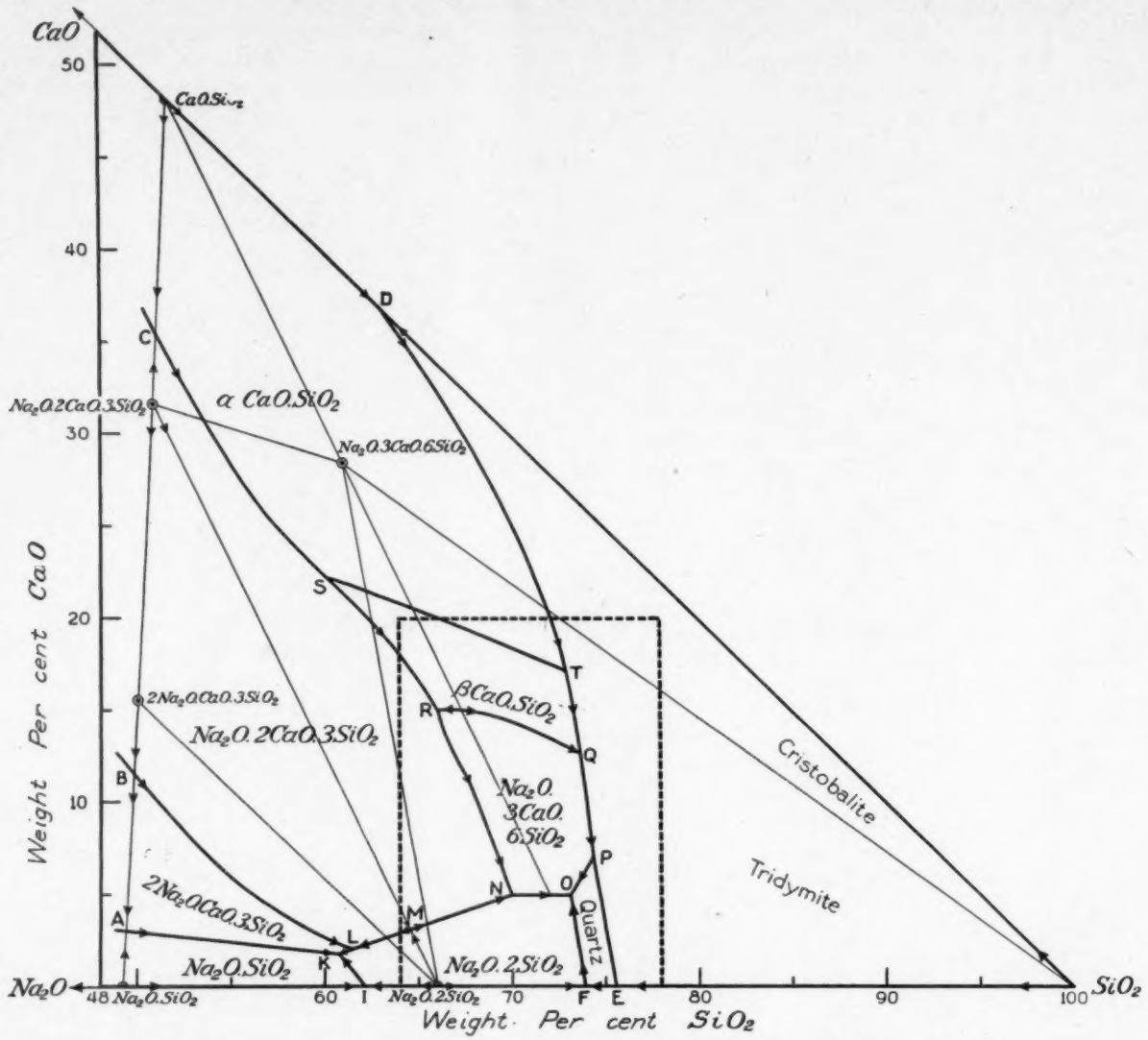

FIG. 6. SKETCH SHOWING THE BOUNDARY CURVES AND TIE-LINES OF FIG. 3 IN RECTANGULAR COORDINATES.

is to the left of the above line, the secondary phase is $2Na_2O.CaO.3SiO_2$, and the liquid follows the boundary, BL, until the point, L, is reached. Here the reaction

$$L + Na_2O.2CaO.3SiO_2 = 2Na_2O.CaO.3SiO_2 + Na_2O.2SiO_2$$

takes place until the mixture has solidified completely. If the original mixture lies to the right of the line, L-Na_2O.$2CaO.3SiO_2$, the same three phases are finally formed, but $Na_2O.2SiO_2$ is the second crystalline phase to separate, and at L the liquid of composition L reacts with the primary phase to form $Na_2O.2SiO_2$ and $2Na_2O.CaO.3SiO_2$.

Glasses whose compositions lie within the field of Na_2O.$2CaO.3SiO_2$, and also within the triangle, $Na_2O.2SiO_2$-$Na_2O.2CaO.3SiO_2$-$Na_2O.3CaO.6SiO_2$, all solidify completely as a mixture of these three crystalline phases, but the crystallization paths differ according to whether the composition is to the right or left of the line, N-$Na_2O.2CaO$.$3SiO_2$. If to the left of this line, the second phase to appear is $Na_2O.2SiO_2$, along the boundary MN, and the residual liquid follows the line MN to the reaction point N. Here the reaction $Na_2O.2CaO.3SiO_2$ + liquid N = $Na_2O.2SiO_2$ + $Na_2O.3CaO.6SiO_2$ takes place, until the liquid has entirely disappeared. If the original composition is to the right of the above line, either $CaO.SiO_2$ or $Na_2O.3CaO.6SiO_2$ is the secondary phase. If separation of $Na_2O.2CaO.3SiO_2$ results in the liquid composition being displaced in such a direction that the boundary CSRN is intersected between C and S, the high temperature form of $CaO.SiO_2$ separates, and should invert at S to the low temperature form; and if intersection takes place between S and R, the low form should separate. In either case, at R the reaction $CaO.SiO_2$ + liquid R = $Na_2O.2CaO.3SiO_2$ + $Na_2O.3CaO.6SiO_2$ takes place, but there must be some residual liquid remaining after all the $CaO.SiO_2$ has disappeared, because by hypothesis the original composition is outside of the triangle formed by the three solid phases. The system thus becomes monovariant, and the liquid follows the boundary curve RN, with simultaneous crystallization of $Na_2O.2CaO.3SiO_2$ and $Na_2O.3CaO.6SiO_2$. At N,

$Na_2O.2SiO_2$ appears, and the system is invariant. Reaction will take place as before, until the liquid has disappeared, and only the same three crystalline phases are left.

It was possible for the above mixtures to solidify completely at N because the original composition was inside of the triangle, $Na_2O.2SiO_2$-$Na_2O.2CaO.3SiO_2$-$Na_2O.3CaO.6SiO_2$, and the liquid was exhausted while some $Na_2O.2CaO.3SiO_2$ remained. If the original mixture was in the field of this compound, but to the right of the tie-line, $Na_2O.2SiO_2$-$Na_2O.3CaO.6SiO_2$, the $Na_2O.2CaO.3SiO_2$ disappears first, leaving liquid of the composition N. Since one of the solid phases has disappeared, the system is now monovariant, and the liquid will follow the boundary NO, with simultaneous crystallization of $Na_2O.2SiO_2$ and $Na_2O.3CaO.6SiO_2$, until at the ternary eutectic quartz appears, and the liquid will solidify completely. If the original composition was to the right of the N-$Na_2O.2CaO.3SiO_2$ tie-line, the first boundary intersected will be CSRN, and the liquid will follow this boundary to the same reaction-point N. The details along this boundary will be discussed subsequently.

Crystallization paths within the field of $Na_2O.2SiO_2$ are simple. If the boundary intersected after passing through the field of $Na_2O.2SiO_2$ is between N and L, $Na_2O.2CaO.3SiO_2$ will be the secondary phase, and the liquid will follow the boundary to L, and at this reaction point $2Na_2O.CaO.3SiO_2$ will appear. If the original composition was inside the triangle, $Na_2O.2SiO_2$-$2Na_2O.CaO.3SiO_2$-$Na_2O.2CaO.3SiO_2$, at L the reaction $Na_2O.2CaO.3SiO_2$ + liquid L = $2Na_2O.CaO.3SiO_2$ + $Na_2O.2SiO_2$ will take place, and the mixture will solidify completely to these three crystalline phases. But if the original composition is within the triangle, $Na_2O.2SiO_2$-$Na_2O.SiO_2$-$2Na_2O.CaO.3SiO_2$, when the reaction takes place at L, $Na_2O.2CaO.3SiO_2$ will disappear, and the monovariant liquid will follow LK, to solidify completely at the eutectic K. If the secondary phase is $Na_2O.SiO_2$, the boundary intersected by the crystallization path will be IK. If the original composition is in the triangle, $Na_2O.2SiO_2$-$Na_2O.3CaO.6SiO_2$-SiO_2, the crystallization path will end at the eutectic O. If the boundary MN is intersected, $Na_2O.2CaO.3SiO_2$ will be the second phase to appear, but it will disappear by reaction at N, then follow NO to the eutectic. If the boundary intersected is FO, quartz will appear, and at O, $Na_2O.3CaO.6SiO_2$.

Glasses in which $CaO.SiO_2$ is primary phase may follow several crystallization paths, depending on the composition, but in all cases the reactions are complicated. Mixtures within the triangle, $Na_2O.2CaO.3SiO_2$-$CaO.SiO_2$-$Na_2O.3CaO.6SiO_2$, will solidify ultimately as a conglomerate of these three phases. If the boundary intersected by the crystallization path is CSR, initial crystallization of $CaO.SiO_2$ is followed by secondary $Na_2O.2CaO.3SiO_2$, and the liquid will follow this boundary to the reaction point R. The reaction at this point, $CaO.SiO_2$ + liquid R = $Na_2O.2CaO.3SiO_2$ + $Na_2O.3CaO.6SiO_2$, continues until one of the reacting phases disappears. When the original composition is within the triangle assumed above, liquid is first to disappear, and the mixture solidifies. If the boundary intersected by the crystallization path is RQ, to the left of the prolongation of the tie-line, $CaO.SiO_2$-$Na_2O.3CaO.6SiO_2$, this boundary is followed to R, and the same reaction takes place as before.

If the original composition is within the triangle, $CaO.SiO_2$-SiO_2-$Na_2O.3CaO.6SiO_2$, but in the $CaO.SiO_2$ field, a similar course of crystallization is followed, with tridymite taking the place of $Na_2O.2CaO.3SiO_2$. The invariant point Q is reached either by the path RQ, in which case $Na_2O.3CaO.6SiO_2$ is secondary phase, or by the path DTQ, in which case tridymite is secondary phase. In either case, at Q the reaction

$CaO.SiO_2$ + liquid Q = $Na_2O.3CaO.6SiO_2$ + SiO_2

proceeds until the liquid has all disappeared.

Every mixture within the triangle, $Na_2O.2SiO_2$-$Na_2O.3CaO.6SiO_2$-SiO_2, crystallizes finally at the eutectic O, but different mixtures take very different courses to reach that point. Those within the fields of $Na_2O.2SiO_2$ and $Na_2O.2CaO.3SiO_2$ have been discussed. Those within the $CaO.SiO_2$ field take the same course which has already been described, to either R or Q. But when the reaction at this point is complete, the $CaO.SiO_2$ will have been resorbed, and some liquid will remain. The system thus becomes monovariant, and follows either RNO or QPO to the eutectic.

Glasses in the field of $Na_2O.3CaO.6SiO_2$ follow a crystallization path along a straight line passing through the compound and the original glass, until a boundary is intersected. If the boundary is RN, the second phase is $Na_2O.2CaO.3SiO_2$, which at N reacts to form $Na_2O.2SiO_2$, as described above, then follows NO, while if the boundary intersected is NO, $Na_2O.2SiO_2$ will crystallize from the melt. In any case, when the liquid follows NO, at the eutectic quartz appears, and these three phases crystallize simultaneously until solidification is complete. If the boundary intersected is QP, tridymite is the phase to appear, and at P it inverts to quartz. The liquid then follows PO, and solidifies at the eutectic.

All the possible crystallization paths have now been discussed, with the exception of those arising in one of the SiO_2 fields. Any such path will intersect either DTQPO or FO, but in either case the subsequent reactions along these boundary curves have been discussed. EP is the transition curve of tridymite to quartz, a constant temperature curve.

The preceding discussion has been predicated on equilibrium being attained in all reactions, but of course it is the failure to reach equilibrium that chiefly makes this system of interest, and glass a possibility. While it is not usually possible to obtain the equilibrium, it does not follow that this diagram does not give information as to the crystallization which will take place. It will rarely be found that the first phase to appear is other than that corresponding to the field within which its composition lies. The only case in which there is a probability of this is in the $Na_2O.3CaO.6SiO_2$ field near the $CaO.SiO_2$-$Na_2O.3CaO.6SiO_2$ boundary, especially near the tridymite invariant point. Here there is a possibility of either $CaO.SiO_2$ or tridymite coming out as metastable phases when glass is cooling down; but such appearance of metastable phases is not to be expected on heating. The failure of the secondary crystallization to appear at a boundary within a given time has often been observed, but it will appear if time be given. The failure of

a given phase to react to form another and stable phase, for example, of $CaO.SiO_2$, to react to form $Na_2O.3CaO.6SiO_2$, or of tridymite to form quartz, has often been observed; but $CaO.SiO_2$ has not been observed on heating a glass within the $Na_2O.3CaO.6SiO_2$ field, nor has the latter compound appeared in the quartz or tridymite field. Metastable crystallization is rarely observed in the $Na_2O.2CaO.3SiO_2$ or the $Na_2O.2SiO_2$ field.

The discussion in this paper has dealt largely with the liquidus temperature, which is of paramount importance in any discussion of the devitrification of glass. It has a definite theoretical significance, and it can, with assurance, be regarded as determined solely by the composition, neither of which characteristics is shared by measurements of the rate of devitrification. It is independent of the thermal history of the glass, and of the presence of bubbles or other possible nuclei. Above this temperature, not only is the separation of crystals impossible, but also the solution of crystals in liquid takes place with evolution of energy. Below the liquidus, however, it is the separation of crystals that takes place with evolution of energy, and in both cases the energy difference between devitrified and non-devitrified glass is the cause of the separation or solution of crystals. The process of devitrification is merely the separation of crystals from a melt, which cannot take place above the freezing point, but below the freezing point takes place with evolution of heat.

Summary

The preceding discussion has dealt with the application of the principles governing heterogeneous equilibrium to the devitrification of glass, and the methods of graphical representation of the phase equilibrium relations dealing with liquids and crystalline solids. The use of such diagrams has been exemplified in detail, making use of the binary system, $Na_2O.SiO_2$-SiO_2, and the ternary system, $Na_2O.SiO_2$-$CaO.SiO_2$-SiO_2, to illustrate the methods of portraying composition in binary and ternary systems, of following the change in composition of the liquid when crystallization takes place, and of following the changes which take place when boundary curves are intersected, and when these boundary curves intersect at several different types of invariant points. It is pointed out that while equilibrium is not met with in those silicate systems of interest in glass technology, nevertheless such phase equilibrium diagrams give information as to the crystallization to be feared with a given glass composition, and the conditions under which it may, or may not, take place.

Geophysical Laboratory,
Carnegie Institution of Washington,
January, 1931.

Glass Technologists of America

G. W. Morey

President of the Glass Division, American Ceramic Society

When we look in the fourth edition, page 693 of the American Men of Science, we see there Morey, George Washington, Washington, D. C.

> "Morey, George Washington, Geophysical Laboratory, Washington, D. C. *Physical Chemistry, Minneapolis, Minn., Jan. 9, 88. B. S. Minnesota, 09. Asst. chem., Minnesota, 07-09; asst. chemist Bureau Standards, 09-12; asst. physical chemist and physical chemist, geophys. lab, Carnegie Institution, 12- Gen. manager, optical glass plant, Spencer Lens Co. 18-20. Manufacturer optical glass, W. I. B. 17-18. Chem. Soc; Opt. Soc, Wash. Acad. Acidimetric, alkalimetric and calorimetric standards; gas at low temperatures; physics and chemistry of high temperatures and pressures; hydrothermal silicate synthesis; optical glass; general silicate chemistry."

Note in the second line of this life history the word oratory as being the other end of the laboratory, the word fortunately being divided in the print in that manner. It must be that the author of this life history intended such a division to be apparent, for beyond being a scientist that is one of the strong characteristics of George Washington Morey. This life history does not go on further to state that Dr. Morey left the Spencer Lens Co., he went back to the Geophysical Laboratory where he has been intensely interested and active in the study of the crystallization of silicate melts and their general peculiarities. Dr. Morey is also the author of the glass portion of the International Critical Tables which have met with universal approval except that unit of kilo-megabaryes which is too technical a unit for most of us to apply. In addition to his interest in silicates George is known for his fondness of landscape gardening, in fact his front lawn is laid out on a phase rule diagram, different varieties of rose bushes representing different crystal components. It is understood that he has used

G. W. MOREY

up all the varieties of plants available, and as substitutes for new crystals has been forced to bring in rather rare varieties of orchids. He has been an active collector of data on birds for the Biological Survey. George is married, has one daughter and lives in Washington but somewhat on the outskirts of the city. The Glass Division members of the American Ceramic feel themselves particularly fortunate in having a man of his caliber at the helm this next year.

Decorative Processes Used in the Blowing Room

By ROY E. SWAIN[1]

TO relieve the monotony and present a greater variety in the selection of glassware several treatments have been devised to add to the attractiveness of the ware. In some cases such treatments are used to conceal bad glass (cords, waves, off-color and so forth) and as such are known as "bad glass" jobs. Some skill is required in the execution of any of the decorative processes that will be discussed but by studying the methods and equipment described, fair results should be obtained in a comparatively short time.

In most factories making blown household ware will be found a number of optic or core molds. These molds are usually made of cast iron or brass as shown in Fig. 1 and vary in size and shape according to the design of the article that is to be elaborated by means of the core mold. Another method of making the fluted optic mold is to assemble a number of fins of sheet metal as shown in Fig. 2. This type possesses some advantages over the castings and is usually less expensive to construct. These molds are made rigid and enough draft is provided to permit the withdrawal of the blank but in the case of the more complicated patterns it is necessary to build hinged sectional molds in order to release the blanks.

In the use of core molds the glass is marvered or blocked and blown out as usual. The blank may be worked smaller than the core mold and by a puff of air blown out to make contact with design of the core mold, or it may be blown slightly larger than the core mold and pressed into contact with the figures to produce the design.

The sharpness or depth of the pattern will vary with the blowing pressure used, the skin thickness of the blank, the amount of time the glass is held in contact with the metal, and the amount of time allowed for reheating before blowing in the mold. Therefore if a uniform pattern is desired it is necessary that the condition of the glass be kept constant and that the shop observe a clock-like schedule.

Fluted optic may be made either straight or spiral. In straight fluted optic paste mold ware the blank is usually worked comparatively cold and the direction of the pipe rotations reversed frequently, that is, the blank is rocked in the mold rather than turned in it.

The spiral optic is produced by working the glass hotter and turning the glass in the same direction until set. The lower portion of the blank blows out to the sides of the mold first and provides a dragging action that causes the blank to twist. In semi-automatic production it is sometimes necessary to provide the twist in the blank before placing it in the mold.

There will be some variation in the pitch of the flutes but a slight variation is not undesirable as it relieves what might otherwise be considered a mechanical appearance.

[1]Huntington Park, California.

CRACKLED GLASS

In hand work the open variety is made by plunging the partly formed blank in water and reheating in a moderately hot fire. As the glass begins to soften it should be given a puff of air to expand it slightly in order to prevent the healing over of the cracks formed by the water. Care must also be taken not to heat the glass too hot as the pattern will then become indistinct and again if the blank is not

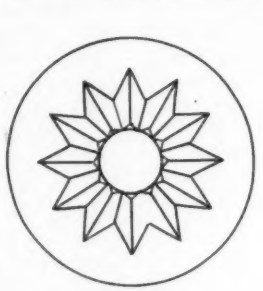

FIG. 1

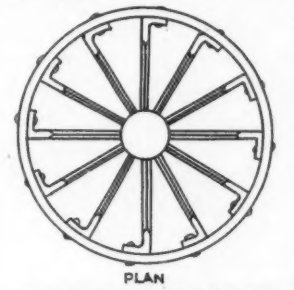

FIG. 2

reheated enough the surface may be covered with sharp points and edges that add to the difficulty of cleaning and make handling dangerous. To add variety to the pattern the blank may be warmed in and plunged in the water two or more times. As in the optic ware a fairly close observance of the shop schedule is necessary to obtain uniform results.

The closed crackled glassware is produced by blowing the article in the mold before plunging it in the water. It is necessary to remove the ware from the mold almost as soon as the mold fills in order to prevent breaking in the water. After being plunged in the water the article is warmed in and reblown in the mold or a former to restore the shape which is usually destroyed to some extent in the crackling.

In both types of crackling the pattern may be made coarse or fine by controlling the condition of the glass and the system of working. Hot glass worked up quickly will produce a fine patterned crackle that gives the surface a lustrous shimmer while with a colder glass the individual crackles

will be larger and more scattered. The softer glasses have a tendency to produce the finer crackles while the harder glasses will produce a coarser crackle under the same working schedule. It might also be observed that the sharper the temperature gradient in the article at the time of plunging into the water the finer and more silken the finish. In the coarser crackles there is always danger that the crackles will be too deep and thus seriously impair the strength of the article and in extreme cases may even break through the inner surface.

BUBBLE GLASS

Some very pleasing effects are obtained in decorative and lighting glassware by means of bubbles enclosed in the glass. A common way to secure these is by means of the batch and melting schedule. In this way the "antique" is more nearly duplicated for we may be quite certain that the ancient glass blowers had many impurities in their batch materials and the melting equipment of those days would hardly be expected to plain even a well laid batch.

A regular pattern of uniformly sized and regularly shaped bubbles may be produced by pricking a number of indentations on the surface of the core or ball before covering. Each of the indentations made in the ball entraps a small amount of air which takes the shape of a sphere. These spheres will flatten somewhat if the glass is blown thin but will remain circular in section parallel to the surface. These bubbles often reflect the light so well that they appear to have been silvered.

A method that is used to produce bubbles more like those in the poorly melted glass consists of dusting the ball or core with one of the volatile batch ingredients, which upon being covered with another layer of glass throws off gas. Due to the irregular size and shape of the dust particles there is a corresponding irregularity in the shape and size of the bubbles.

Bubbles may also be produced by smoking the ball in a reducing flame. The ball must be cooled somewhat below the usual working temperature or the carbon deposit will be spotty and the results uneven. When well made these bubbles are fairly regular in size, shape and distribution. The artificially produced bubbles have the advantage of being well below the surface of the glass and losses through handling and finishing are small.

While tipping was at one time a well-known blowing room art it is a subject that may be better handled under the general heading of fusion of glass to glass.

Among collections of old glassware will be found many examples of two-toned or two-color glass that has been made from a glass capable of color changes when subjected to heat treatments. Such colors are known as heat-developed colors and are occasionally used in the production of novelties for the variety stores. The heat-developed opals are usually found to be light in color when examined by transmitted light but by reflected light appear quite dense in contrast to the transparent clear or colored background.

Polka-dots and spiral flutes are simple designs that are made by means of optic molds and warming in. This produces heavy sections which by cooling more slowly are able to strike the color.

Color contrasts are also produced by first blowing the article and shielding a portion of the article while warming in. The part exposed to the heat will strike color while the protected portion remains unchanged.

Flares, nappies, trays and so forth are often colored only on the edge. This is done by snapping up and warming in, keeping the article only as far in the fire as it is desired to strike the color. These articles are made by pressing.

In another class of pressed ware the weight distribution is used to control the color effects and a number of articles have been devised to utilize the color contrasts that can not be truly known as decorative in purpose. The well-known red and yellow signal glassware is perhaps the best example of this type of color contrast. In this glass the red strikes only when cooled slowly so the article is made heavy where the red is desired and light where yellow. By pressing, the light sections are cooled almost instantly; the heavier sections cool slowly.

Another line of glassware known as onyx or agate is produced in several different ways. Some colored glasses will, when chilled quickly in the melting unit, strike a number of colors varying with the temperature and time. By gathering the colder glass off the top and by mixing the different strata into the gathering an endless variety of color combinations and patterns are produced. Such glasses are too viscous for the manufacture of other than the very heavy pressed ware like ash trays, desk sets and paper weights.

Variegated colors are also produced by ladling the separate colors on to the surface of the base color or glass whereby skilful gathering the color combinations and design may be held to within fairly close limits. To assist in this class of work, pot rings have been devised to control the flow of the imposed glasses. As these glasses may be worked at almost any desired temperature they are suitable for blown as well as pressed ware.

Built-up variegated colors of a different type are often seen in blownware displays. Bits of colored glass are marvered into the core and over this is gathered a layer of crystal glass. The core is usually of some translucent or opaque color to give a suitable background for the many colors used.

IRIDESCENT GLASSWARE

There are several grades of iridescent glassware, each being a result of some variation in the system or method of manufacture. This effect is produced by coating the glass with a film of some metallic salt such as tin chloride or iron chloride. Different methods have been devised for applying this film. In the manufacture of very heavy pressed ware it is possible to dissolve the salts in water or acid and apply the solution by means of an atomizer as the glass reheats when first removed from the mold. In case there is not sufficient heat in the article to complete the reaction a moderate fire is used to reheat the glass and the spray applied in the flame. The article should be rotated or otherwise kept in motion. By this method a deep velvety finish or metallic luster may be obtained. This finish is especially striking when applied to a deep colored or opaque background. A very light film gives an effect that resembles the colors of a soap bubble.

Another method of applying iridescence to glass is to expose the hot glass to fumes produced by heating these salts in a crucible. The crucible is placed in a "dope box" to conserve the fumes and protect the workman. As the fumes cause a nose and throat irritation that may result in a permanent injury, great care is necessary to exhaust the fumes to the open air.

In some very light blownware it has been possible to apply the iridescent finish to the inner surface of the glass during the process of manufacture but the effectiveness is destroyed to some extent, especially in the case of hot mold ware, by the reflection of light by the outer surface of the glass. The greater amount of the thin blown ware is annealed and finished before being treated. The solution when applied cold has a tendency to form small beads which upon drying leave specks or ringlets of a heavier deposit while the hot application produces a smoother, better distribution.

Some finishing operations may be considered as ornamental or decorative. A great many shapes are desired that cannot be produced by any of the simple methods of glassworking but by adding another shop operation may readily be produced. An article may be partly formed in a mold and a portion reheated and by shearing, finishing tools, or especially designed equipment worked to the proper shape. Flaring, cutting down, cupping, and swinging out, are well known examples of this type of work. Often as many as four or five distinct shapes are made in the same mold.

Only the simple processes have been considered but from these some suggestions may be gained for increasing the variety of glassware produced without adding greatly to the outlay for factory equipment.

The Fluorescence of Certain Colored Glasses

W. R. LESTER*

DURING the course of some experimental work on the action of ultra-violet radiations on pharmaceuticals it was observed that certain of the containers used exhibited fluorescent properties. It was thought desirable to expose samples of different colored glasses to the ultra-violet in order to determine whether or not the property of fluorescence could be used as a qualitative test for the coloring compounds in the glasses.

All the glasses tested were of the soda-lime-silica type and the majority consisted of colored bottle glasses found on the market with the exception of a few special glasses that had been made in the laboratory.

The samples were placed below the rays of a quartz mercury arc lamp equipped with a Woods filter (opaque to visible light and transparent to the near ultra violet) and the fluorescent properties noted. Table I gives the descriptions of the glasses and the results.

From the results it is seen that the following separations may be made:

1. It is possible to distinguish between glasses decolorized with selenium or manganese. The time required is only a fraction of the time necessary to determine the elements by qualitative chemical analysis.

2. It is usually possible to pick out greenish blue copper glasses from those colored by iron-cobalt or chromium cobalt by visual inspection but if the glasses were of approximately the same shade a visual inspection would perhaps be difficult. The different glasses are then very easily separated by means of the fluorescent property of the copper glass. It is unfortunate that neither the iron or chromium glass gives a characteristic fluorescence. This applies also to the green glasses where the uranium glass is the only one of the three that shows this property.

3. As seen above it is possible to detect manganese in decolorized glass. It also can be detected in a blue glass containing both cobalt and manganese providing the color of the glass is not so dark as to mask the feeble fluorescence.

4. Cerium may be detected by its light purple fluorescence but here again the resulting color is affected by other agents as in the case of the glass containing both cobalt and cerium.

5. The amber glasses fall into three groups: the first giving an orange fluorescence, the second a dull brown, and the third no fluorescence. Out of about fifty glasses tested about 25 per cent were in the first group, 25 per cent in the second group and the remainder in the third group. The coloring agents used in the glasses were not known but it is probable that those showing the orange and dull brown fluorescence contained sulphur in some form as evidenced by the fact that a glass containing cadmium oxide shows no fluorescence while glasses containing cadmium sulphide as the coloring agent shows an orange fluorescence.

The results clearly indicate that several of the different coloring agents may successfully be detected by means of their fluorescent properties.

Table I

No. of samples tested	Description of the glasses	Coloring agents used	Color of the fluorescence
3	Flint bottle	Manganese[1]	Light green
2	Petri dish	Manganese[1]	Light green
25	Flint bottle	Selenium[1]	No fluorescence
2	Blue green	Iron and cobalt	No fluorescence
3	Blue green	Chromium and cobalt	No fluorescence
2	Blue green	Copper oxide	Green
10	Green	Iron oxide	No fluorescence
3	Green	Chromium	No fluorescence
2	Green	Uranium	Green
10	Blue	Cobalt	No fluorescence
3	Light blue	Cobalt and manganese	Dull green
3	Dark blue	Cobalt and manganese	No fluorescence
2	Blue	Cobalt and cerium	Lilac
3	Flesh	Cerium	Light purple
2	Canary yellow	Cadmium sulphide	Orange
10	Amber	?	Orange
10	Amber	?	Dull brown
20	Amber	?	No fluorescence
2	Opal	?	Dull purple
1	Red	?	No fluorescence
1	Green tint	Cadmium oxide[2]	No fluorescence

[1] Decolorizer.
[2] Does not impart color to this glass.

* Chemist, Maryland Glass Corporation.

The Manufacture of Rolled Plate

By ERNST LUTZ*

(*Continued from the March, 1931, issue*)

This work has been revised, so far as the English and the technical expressions are concerned, by F. W. Preston, who has also added a number of notes relating in general to the special conditions of American practice; but it must be understood that the opinions expressed in the text are those of Mr. Lutz, and neither the Editor nor Dr. Preston accepts responsibility for them.

Inserting the Rough Plate Into the Oven

For the insertion of the rough glass sheet into the annealing oven, sliding shovels as shown in Figs. 101 and 102, and called stowing tools, are used. They are built up of a cross girder (a) consisting of wood, angle iron or iron tubing, and are equipped with handles b and a hook c to connect up with the pulling ropes. On to this cross girder a frame d built of iron tubing or angle iron is added; the front cross rod e of this frame b is of U-section and during the stowing process embraces the head edge of the sheet. The cross rod e is further lined with a thick layer of asbestos so that the sheet edge finds an elastic abutment and comes in contact at all points; by this means the sheet is also protected from direct contact with the cold iron of the rod. As soon as the asbestos, through frequent use, is getting hard, it has to be slackened or renewed, as otherwise the sheet edge may develop cracks, which in the lehr will extend further and may cause the breakage of the whole sheet. This precautionary measure is of first importance. The cross beam a rests on two broad rollers f, made of soft metal, such as bronze or copper, which attack the surface of the casting table as little as possible. The cross girder itself is preferably made of wood, so that it shows some elasticity and at the same time has sufficient weight to prevent the shovel, when being pulled, from tipping upwards. If this should happen during the insertion, one man on each side has to come in and press the handles b.

When coming in contact with the rough glass sheet, the shovel lies on the girders g, which consist of angle iron or wood. The upper surface of these girders, i.e., their sliding surface, has to be at such a level that the rollers f meet the table without any shock. As described before, the first threads of the rope drums in the roll winch, which are winding the pulling ropes of the shovel up, have a smaller diameter than the rest and only gradually, and in a spiral form, increase up to the full periphery (Figs. 62 and 66). In consequence thereof the insertion is started quite slowly and only gradually reaches the full velocity of about 5 feet per second.

The insertion is started as early as possible and as soon as the part of the sheet adjacent to the head has become sufficiently rigid to withstand the great pressure exerted without distortion; further the far end of the sheet has to have assumed a certain rigidity, so as to allow of pushing with safety. The later the insertion is started, the colder will be the end of the sheet which is rolled first and the greater will be the danger of cracks, making it useless, or even causing the fracture of the sheet in the lehr, or after its exit from same. Finally excessive stresses may arise, which will not equalize entirely in the lehr. As mentioned before, it is an unfortunate coincidence that the top layers of the pot content, i.e., the coldest part of the glass mass, form the sheet head, whilst the core of the glass, i.e., the hottest and most liquid parts, will form the tail end of the sheet; this core maintains its temperature in the glassheap pushed in front of the roll, almost without loss to the very end, and the tail end takes quite awhile to get sufficiently stiff for stowing. Generally speaking, the core represents the purest and most perfect part of the pot content and in consequence the tail of the sheet usually shows the highest quality.

The more liquid the glass, the longer will it take until the tail end has become strong enough; on the other hand with a more viscous glass mass the head of the sheet will congeal faster. In between those extremes the most favorable middle course has to be found. With a thickness of 3/8 to 7/16" the time interval between the arrival of the roll at the roll-winch and the beginning of the insertion is normally about 18 to 22 seconds.

If it happens frequently that in spite of one end of the sheet becoming strong enough in time, its opposite end will still distort when inserted, the sheet is held down by the cross rods h (Fig. 101 and 103) which are pressed on the dangerous spots of the glass, so as to prevent the formation of humps. On each side of the table a man follows, pressing down the long handle of the beam h with the weight of his body. This expedient has proved successful. However, it requires great force and alertness on the part of the two men, as the beam h has to be lifted up, immediately in front of the roll winch, so that the shovel can slide through without throwing it against the roll resting on the roll winch, a proceeding which might damage the latter. This device could also be made automatic.

On the roll winch the cross beam a strikes a lever, which shuts the electric-motor off automatically. This lever has to be so set that the movement of the shovel is interrupted in time to avoid the cross beam hitting the roll and to avoid the rough glass sheet overshooting the mark and striking the opposite wall of the lehr; the length of the frame d has to be dimensioned accordingly. In order to protect the roll in any case from damage, which would cause unevenness and imperfections in the sheet, the cross beam a is fitted with

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* Of Desseau, Germany. This work will appear in German in the forthcoming new edition of *Dralle-Keppeler*, "Die Glasfabrikation," due this year, about July. The GLASS INDUSTRY probably will by that time have completed the English translation, with some comments on its applicability to American conditions by F. W. Preston.

FOOTNOTE: In the Figures, originally prepared for use eventually in the coming new edition in the German language of *Dralle-Keppeler*, "Die Glasfabrikation" in 1931, dimensions are given in metres (*m*) and millimetres (*mm*). We would like to have given these in feet and inches but the translation and the making of nearly two hundred and fifty new illustrations would have involved a prohibitive loss of time and expense. To some of our readers the metric system is as familiar as the English units; for the others we may say that a metre is approximately 40 inches, and a millimetre is approximately 1/25 of an inch. A thousand millimetres, of course, go to a metre.—*F. W. P.*

buffer i made of rubber or felt; it is further advisable to fix the hooks c flexibly to the cross beam. The stowing tool is returned by hand* to its initial position on the sliding rods g.

In the annealing oven the rough glass sheet is subjected to

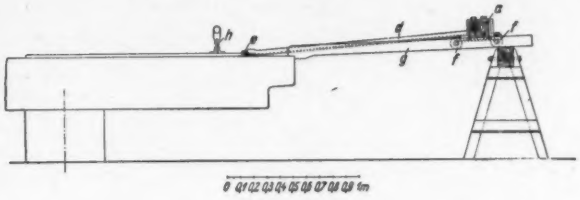

FIG. 101

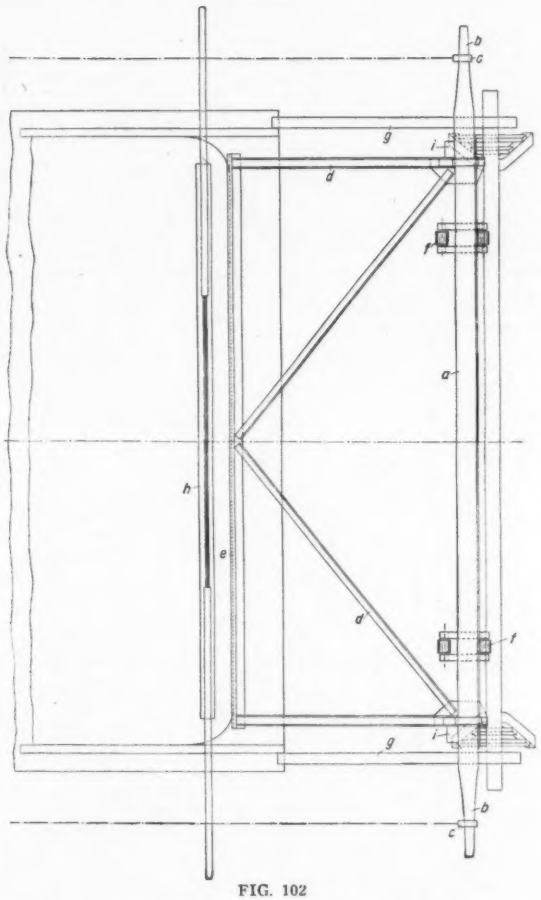

FIG. 102

such a temperature that all its parts are heated up to a point where they make close contact with the plane bottom of the lehr, and where distortions and dangerous stresses caused by its unequal cooling on the casting table are evened out; in other words the sheet must be annealed. However, at no place must the sheet be made so soft and flexible that it follows the small pits which are invariably present in the bottom of the lehr; it should rather remain stiff enough to bridge over small fissures, pits and small hollows left by inadvertence when readjusting the bottom of the oven. Depending on the design of the oven, an initial temperature of 1,150 to 1,300° F. is aimed at.

The remaining problem is the cooling down of the sheet from these temperatures to room temperature without local chilling and with the temperature of all parts of the sheet declining at the same rate, so that the plate cannot crack, or get new and dangerous stresses that may cause warping. Between 1,000 and 1,100° F. lies the so-called critical temperature range, within which the structure of the congealing glass reaches a certain finality. This temperature range is reached or even undershot by the head of the sheet, before the tail end is even rolled. For this reason alone an equalizing of the stresses within the sheet cannot take place without annealing; part from this great discrepancy between sheet head and tail and temperatures, the freshly rolled sheet, left on the casting table or in the open room would, within a few minutes, distort at numerous spots and break into a great number of small pieces, because of the rapid cooling down and lack of time to equalize additional stresses formed everywhere within small areas.

After the annealing, i.e., after the removal of the stresses, the cooling process should be carried on in such a way that the sheet is subjected over its entire area to equal temperature reductions, which prevent the generation of new stresses. If this requirement should be completely fulfilled, the sheet might be cooled very rapidly without taking harm; even in this case, however, above the critical temperature range and particularly within this range itself, chill effects would have to be avoided, as the glass in this state is very sensitive and the cooling curve should be kept very flat. Existing ovens will fulfill these requirements only approximately, and after annealing new stresses sometimes arise. The cooling down must therefore be so gradual that sufficient time remains for eliminating, or at least for minimizing, these inequalities.

Formerly it was the general practice to cool the rough plate glass sheets in single-chamber annealing kilns, which offered room for one, or at most two sheets; annealing kilns were also built to hold four sheets; but almost universally there were chambers for only a single sheet. Such chambers are heated up for 6 to 10 hours before casting; after the sheet is inserted the whole chamber, with the sheet inside, is cooled down and only the next day or day after is heated up again for a fresh sheet. In most plants the temperature variations in these chambers were so great and the process of cooling down so complicated that it was necessary to cool very slowly, and the sheet remained for more than a day and sometimes for forty and even more hours in the annealing kiln. Such an oven could evidently only be recharged every second day with a new sheet; the rough glass factory therefore required twice as many annealing kilns as pots in commission. In addition further kilns had to be kept as stand-bys in case of necessary repairs. However, as time went on it was found possible to cut the time

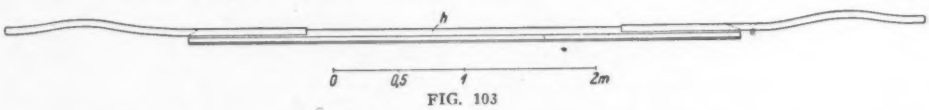

FIG. 103

* By power in American practice.—F. W. P.

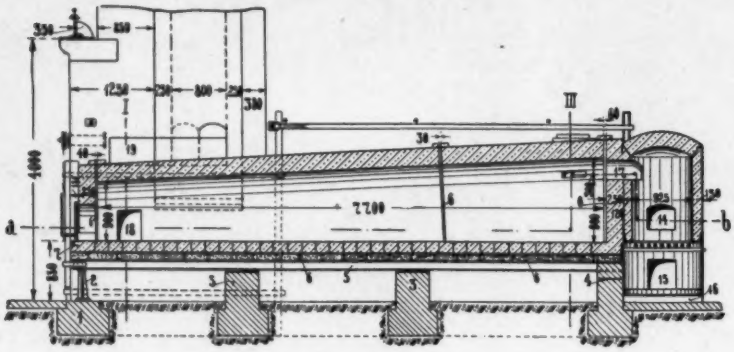

FIG. 104

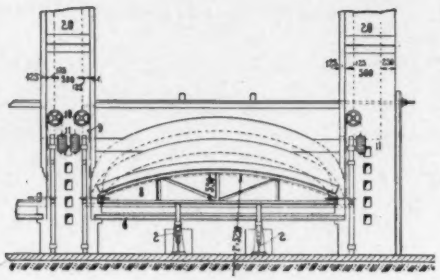

FIG. 105

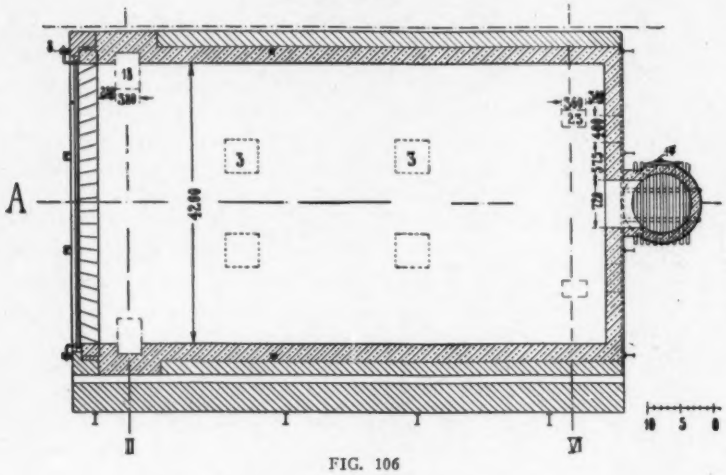

FIG. 106

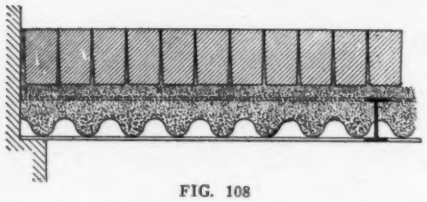

FIG. 108

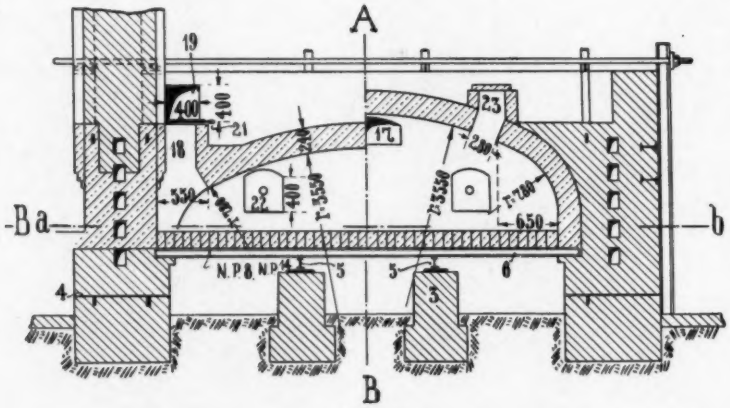

FIG. 107

of cooling down to about 15 to 16 hours without any disadvantage to the rough glass sheet; the kilns were thus ready again next day and sufficient time was left to heat them up for the next casting. Apart from 2 to 3 stand-by kilns, there were now only as many annealing kilns required as pots were standing in the furnaces.

This meant a great saving in room, floor space and cost of plant. Continuous lehrs, as commonly used for ordinary glassware, have, on account of the size of the rough plate glass sheets, been adopted only during the last 30 years or so and first in the United States of America; today these lehrs are standard and rough glass factories with single chamber annealing kilns quite exceptional;* in some works these old cooling ovens are still kept as stand-bys.

Figs. 104 to 107 show a small single chamber annealing kiln for rough glass sheets of 21 to 23 feet length and 12½ to 13½ feet width. At its rear wall it is provided with a plain grate for solid combustibles and at the front end, where the rough glass sheets are inserted, a flue for the waste gases is arranged at each corner. Arch and oven bottom rest on two foundation walls, which run the full length of the kiln, and at the same time form the partition and supporting walls for the two adjacent kilns. With the

*None in America.—F. W. P.

aid of iron girders, running in a longitudinal direction, small iron cross girders are placed with gaps of 1 to 1¾"; the space between them is filled up with concrete. This concrete must expand as little as possible under the influence of heat and should not distort. It is therefore made of best cement and crushed volcanic pebbles. Still better is a loose fill of crushed pot shell of 1/100 to 1/50" grain size; instead of the pot fragments, infusorial earth is sometimes taken. To support these fillings sheet iron (preferably corrugated sheets) are used, and put on the flanges of the iron cross girders (see Fig. 108). On the concrete or rather on the fill, fire bricks on end are set in sand, or better in pulverized clay or infusorial earth; they are thus only loosely embedded and from time to time, or if any irregularities should develop, they can be re-aligned with a straight edge, so that the bottom always forms as perfect a plane as possible. The opening in the front wall, which extends across the full width of the chamber, can be shut by a sliding door moving up and down in guide-slots. This door is usually built of a wrought iron frame covered with fireproof brick; its weight is balanced by counter weights.

FIG. 109

For the heating, combustibles, usually briquettes, are used which yield long flames, in order to carry as much heat as possible to the farther end of the chamber. The highest temperature is usually reached in a zone of 3 to 7 feet distance from the fire arch, while the opposite end of the chamber remains coolest. The head of the sheet, which is rolled first and which is its coldest part, therefore comes into the coldest zone of the lehr, while the relatively soft end of the sheet meets the hot zone; just the reverse conditions would be desirable from the point of view of the quality of the sheet, of its evenness and of the most satisfactory annealing. It has therefore been suggested that the sheet might be rolled in the direction opposite to the standard, i.e., to run the roll from the kiln towards the opposite end of the table, and to fold the first-rolled head of the sheet immediately after its production and while it is still warm, round an iron bar, and then to pull the plate into the kiln with the aid of two pushing rods, guided on the table sides and gripping the said bar.

With this procedure it would be possible to bring the cooled head of the sheet into the hot range of the fire; however it has never been applied and it must be assumed that the drawbacks represented by the bar sealed into the glass of the head edge and the troublesome arrangement of the pushing construction, overweighed the advantages promised.* Improvements were rather sought in the uniform distribution of the heat by favorable arrangement of the fire and by the form of the chamber. As a first step the fire bridge was made very high, and the fire port placed immediately below the crown; further, in many cases the crown was given a slope as shown in Fig. 104 and the flues at the nearer end at both sides of the chamber were arranged as low as possible, so that the combustion gases at the back of the chamber had to pass high above its bottom and gradually to sink down to the latter in coming forward. In other cases the vault itself was left horizontal, while the bottom was given a pronounced slope towards the grate (slope about 1:14). Frequently kilns were used which, besides the main fire at the back, also had separate fireplaces in one or both corners of the front end, the flues being situated more towards the inner chamber, which was made correspondingly broader. These front fires did not bring any advantages. The best results have always been obtained with chambers having one fireplace at the back wall, two flues with low ports in the front corners and the sloped arch or bottom, as described above. A really uniform distribution of the heat, or what would be more desirable still, such a distribution that more heat would flow towards the front than to the back, has, however, never been attained. The chambers always remain warmest at the rear and consequently the rough glass sheets took a form as exaggeratedly shown in Fig. 109; the edges of the sheet head bent upwards like a dish, while at the sheet end they bent downwards like a watch glass. A more uniform heating of these single chamber annealing kilns would have been obtained by the use of liquid or gaseous fuels, since with these a greater number of nozzles or burners might have been distributed suitably all over the chamber. This way of heating was actually aimed at; the introduction of the modern lehr, however, prevented its complete development.

(To be continued)

*A somewhat similar scheme reaping the advantages mentioned is in use in some American wire glass plants.—F. W. P.

Uses of Nickel

THE PHYSICAL PROPERTIES OF GLASSES IN RELATION TO THEIR COMPOSITION. THE TRANSPARENCY OF GLASS IN THE ULTRA-VIOLET, VISIBLE AND INFRA-RED RANGE.

A comprehensive study was made of the relation between composition and transparency of glass for various ranges of 3. The transmitted spectrum was determined in the ultra-violet by a quartz spectrograph, in the visible by a Konig-Martens spectro-photometer and in the infra-red by a mirror spectrometer with thermocouple and galvanometer. Fifty-nine sets of curves are given of the spectrum as a function of the composition. Mention of glass colored by NiO. The literature on the subject is exhaustively reviewed.

FRITZ-SCHMIDT, M., GEHLHOFF, G. and THOMAS, M. Zft. tech. Physik, v. 11, 1930, pp. 289-326. Chem. Abstracts, v. 24, November 20, 1930, p. 5635.

SEALING METAL TO INSULATING-MATERIAL. A ring or disc-shaped metal member arranged to be sealed to an insulating member of material such as glass consists, at least at the point of sealing, of an alloy containing nickel and one or more of the metals tungsten, molybdenum, tantalum, vanadium, niobium, cobalt, and silicon the coefficient of expansion of the alloy being equal or substantially equal to that of the insulating material to which the metal part is sealed. Preferably the nickel content exceeds 50 per cent of the alloy. One or more substances such as chromium, aluminum, or magnesium, which facilitate the formation of a coherent film of oxide, may be added to the alloy, preferably in a quantity less than 5 per cent. Example of a wireless transmitting-valve, provided with an anoxd consisting of a nickel-tungsten alloy which is sealed to the glass wall portion.

Dicker, British Patent 337,086. Appl. August 6, 1929. Issued: December 17, 1930.

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Columbus' Blunder

Whatever we may think of Columbus as an adventurer, it is certain he was a mighty poor business man. And whatever we may think of the King of Spain who backed him up, it is certain that no American financier would have done so: he would have had a better business head.

The present worth of these United States is given as four million million dollars.

It is generally conceded by our financiers that money ought to yield five per cent per annum with perfect safety: this is conservative investing. Their banks commonly exact six per cent from the poor business man.

If Columbus had had two thousand dollars in 1492, it would have amounted to four million millions, the value of the United States, by 1930, at 5 per cent interest.

Now he could not have bought his ship for $2,000, still less have provisioned it and paid his men. He must have spent a good deal more than two thousand dollars, and John Cabot, Walter Raleigh, the Pilgrim Fathers, and untold others also spent good European money on America.

It was all a ghastly mistake. Columbus would have done much better not to risk his ship, but to have stayed at home and invested his money in safe securities at five per cent, like our modern financiers.—F. W. P.

Ancient British Glassworks Discovered

S. E. Winbolt, well-known British archeologist, reports that at Malham Ashfold, between Wisborough Green and Loxwood, near the north-west boundary of Sussex County, the remains of an ancient glassworks has been unearthed. This affords a valuable addition to extant knowledge of the glass industry in southern England. The extent of the industry has been little known, and so late as 1853 the only Sussex site known to W. H. Blaauw, a famous archeologist of the time, was that at Wisborough Green.

The rarity of glass-making in Britain and its concentration in Sussex were matters of remark in the sixteenth and seventeenth centuries, although recent discoveries have improved the extent and accuracy of existing knowledge. One Thomas Charnock (1557) wrote in crude verse:—

"As for glassmakers, they be scant in the land,
Yet one there is, as I do understand,
And in Sussex is his habitation,
At Chiddingsfold he works of his occupation."

Camden also (1605) and Evelyn (later in the 17th century) remark, with a rough accuracy, that Sussex was the only county in which glassworks were located.

Government interference with an industry is well illustrated in the case of glass. James I issued a stern proclamation forbidding the "melting of glass with timber, or wood or fuel made of the same," but its futility is proved by the fact that glassworks increased afterwards. No doubt glass and iron together were depleting forests too rapidly.

The next government move was one for the protection of the industry. It was recognized that glass was a Sussex (and Surrey) manufacture and all foreign glass was prohibited (1633), although an exception was made in favor of Venetian glass, a monopoly of the import being granted

to one Sir C. Maunsel. So we find in 1656 the Rev. Giles Moore, of Horsted Keynes, buying "4 Venetian glasses" from a traveller for 2s. (50 cents).

The most important factory was at Chiddingsfold, which dates back to before 1240. It provided King Henry III. with both white and colored glass for his Abbey of Westminster. Around the green were 11 glasshouses in the time of Queen Elizabeth, but their working was soon prohibited on a petition of the inhabitants complaining of them as a nuisance. During the Great War their refuse proved a blessing, for the slag heaps were used for road metal, and the roads round Cranleigh village glistened with the Elizabethan by-product.

The Peyk family, who were glassmakers in Sussex from 1435 to 1617 were perhaps the last of this line. At the glasshouse near Alford two French glassmakers, Carre and Tyzack, worked during the latter half of the sixteenth century. An example of Somersbury glass, a fine Jesse-tree window, existed in Cranleigh church before 1798, but it was later destroyed.

In the new excavations at Malham Ashfold there is at present nothing to date the glassworks. There are many pieces of sandstone crucibles, and Mr. Winbolt himself dug from about a foot under the surface pieces of crude glass, clinkers, and bits of sandstone burnt red. The works were on the top of the western slope of a wooded haner, so that the draught from the furnaces was from the east. At the bottom of the gill is a stream, such as flows by all the glassworks mentioned above. Reconstructed from pieces, a crucible has a base with a diameter of 8 in. and height of about 9 in. At the thinnest parts of the base and wall it is 1 in. thick, and at the thickest, at the angle of wall and base, 1⅞ in.

Variation of Viscosity with Temperature

THE variation of viscosity of glass with temperature is a subject that has engaged the attention of the glass industry for some years past. The law connecting the two has not yet emerged, in spite of the considerable amount of experimental work that has been done.

There is therefore the more interest attached to a letter from Prof. E. N. da C. Andrade, of University College, London, which appeared in *Nature* last year. This we reproduce below:

It will be observed that the law proposed by Prof. Andrade is identical with that originally proposed by F. Twyman for the viscosity of glasses near the annealing temperature. Mr. Twyman expressed the viscosity in the form

$$\eta_0^{\frac{T-T_0}{10}}$$

which is identical with the exponential form, though expressed somewhat differently.

Unfortunately the law does not hold very well over a wider range of temperatures in the case of glass, and the real law must be more complicated.

Dr. Fulcher of Corning, in the American Ceramic Society's *Journal* (1925, Vol. 8, p339) showed that for sodium silicate the law could be empirically written, to a first approximation as

$$\eta = Ae^{b/T^2}$$

or to a closer approximation as

$$\eta = Ae^{b/T^{2\frac{1}{4}}}$$

Unfortunately, such a law seems physically meaningless, and further it does not hold good for technical glasses, containing lime or magnesia as well as soda and silica. For these the empirical law of roughly the same form often approximates remarkably close to

$$\eta = Ae^{b/T^4}$$

over a very wide range of temperatures. For this law too, there seems no physical basis, while the law of Twyman, or of Andrade, is more or less what one would expect on the basis of the quantum theory.

H. Schulz, for instance, in the *Keramische Rundschau*, (1925, Vol. 33, p. 395) arrived on theoretical grounds at the formula

$$\eta^2 = \frac{A}{\gamma}\left(e^{\frac{\beta\nu}{T}} - 1\right)$$

where γ is the frequency of the "specific vibration" of the heat absorbing atoms.

The quantity $\frac{h\nu}{kT}$, where h is Planck's constant, k the Boltzmann constant, T the absolute temperature and γ the frequency of the radiation considered, is a quantity that comes in very often in modern physics. The exponential

$$e^{h\nu/kT}$$

is understandable, and it is no doubt with this quantity that the laws of Twyman or Andrade should be expressed, the effective value of γ being therefore calculable, and presumably indicating an absorbing band in the spectrum of butyl alcohol or glass as the case may be. But the more elaborate formulae are seemingly meaningless as they stand. The easiest assumption is, that the glass has a number of absorbing bands, or has only partial transmission over the whole spectrum, so that we have to integrate the transmission over the whole range of values of the frequency in order to get the net viscosity. On this basis the viscositv of any glass at any temperature ought to be predictable if we have a complete spectral transmission curve throughout the visible, ultra-violet, and particularly the infra-red.

There would seem to be scope here for some fundamental research of great value.

Gas-Tight Sealing of Metal to Glass

A coefficient of expansion, for the metal, some 5% lower than that of the glass, favors the production of a gas-tight seal on cooling. If the outer layer of the wire is of Cu, this can, by suitable treatment, be caused to dissolve in the surface layer of glass to give a very good seal. When metals of low expansion coefficients such as Mo or W are used, it is necessary to have recourse to special low-expansion glasses, such as Pyrex, either for the whole of the apparatus or for the first member of a graded seal. Ni-chrome alloy wires up to 0.4 mm. diam. can be sealed directly into Pb glass, and will carry currents up to 2 amp. without trouble. Aschermann, G., Glas u. App., v. 10, 1929, p. 115. J. Soc. Glass Tech., v. 13, p. 230A. Chem. Abstracts, v. 24, September 20, 1930, p. 4602.

New Photoflash Lamp

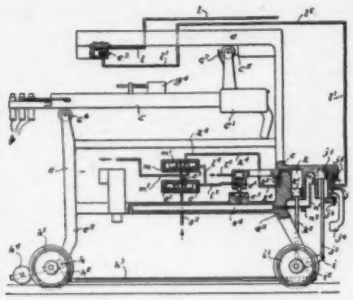
During the past year a new development in the field of photograpy, incorporating a radically new principle in lamp making— a photoflash lamp, was brought out by the General Electric Company. It delivers a high intensity of Neon light. The light-giving element is a 1-in. diameter glass tube 18 in. long and the unit has a maximum overall length of 28 in.; delivering approximately 25 beam candle power per inch length of arc tube.

Recent Patents

NEW INVENTIONS DESIGNED TO IMPROVE GLASS AND THE MEANS OF PRODUCING IT

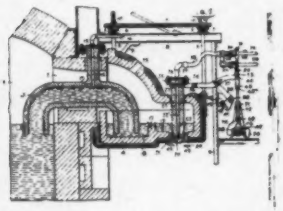
Complete copies of U. S. Patent Specifications may be obtained from the Commissioner of Patents, Washington, D. C., Price 10c each

MANUFACTURE OF GLASSWARE. U. S. 1,790,633. Jan. 27, 1931. Pierce Arbeit, Paris, France, assignor to The Hartford-Empire Company, Hartford, Conn. Filed 4/21/26.

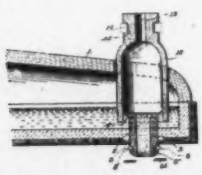


A glass working machine comprising a plurality of split finishing molds arranged in alignment, means for opening and closing said finishing molds by pivotal movement around a horizontal axis displaced vertically from said finishing molds, a like number of suction-fed split parison molds, and means for opening and closing said parison molds by pivotal movement around a vertical axis displaced longitudinally with respect to said finishing molds.

APPARATUS FOR MAKING PLATE GLASS. U. S. 1,792,636. Feb. 17, 1931. John H. Fox and William Owen, Pittsburgh, Pa., assignors to Pittsburgh Plate Glass Company. Filed 10/24/29. In an apparatus for making a sheet of glass, a roller lehr section mounted for bodily movement in a longitudinal direction, means for driving the rolls of the lehr, a pair of sizing or forming rolls mounted in fixed position above the roller bed of said section, means for moving said lehr section forward during the rolling of a sheet and moving it backward after the rolling operation, a bar lehr section in alignment with the roller section comprising spaced bars, means for giving the bars an intermittent movement back and forth and for raising and lowering them, and means between the ends of the two-lehr sections for transferring a glass sheet from the roller section to the bars of the bar section when the roller section moves forward.



GLASS FEEDING MECHANISM. U. S. 1,790,984. Feb. 3, 1931. Everett S. Greer, Zanesville, O., assignor to Hazel-Atlas Glass Co., Wheeling, W. Va. Filed 3/3/27. The inventor has discovered that by employing a bushing which projects upwardly above the floor of the flow spout, and vertically adjusting the bushing so as to alter the upper end of the bushing with respect to the glass level, that it becomes possible to regulate and control to a very fine degree, the shape, weight and size of the glass charges; thereby providing a more sensitive control of these characteristics than has been possible heretofore.



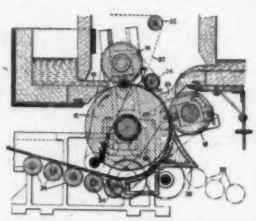
SHEET-GLASS APPARATUS. U. S. 1,796,836. Mar. 17, 1931. John L. Drake, Toledo, O., assignor to Libbey-Owens-Ford Glass Company, Toledo, O. Filed 3/2/27. In sheet glass apparatus, a receptacle containing a mass of molten glass, means for drawing a sheet therefrom, lip tiles covering a portion of the receptacle at opposite sides of the sheet, members of substantially greater width than height arranged at opposite sides of the sheet and covering those portions of the receptacle not covered by the lip tiles, and means for controlling the temperature of said members.

GLASS AND METHOD OF MAKING. U. S. 1,789,658. Jan. 20, 1931. Max Meth, Pittsburgh, Pa., assignor to Isaac R. Stewart, New York. Filed 2/4/27. A glass having a relatively low coefficient of expansion comprising usual constituents of soda, lime, silica glass with a small percentage of a beryllium compound therein.

APPARATUS FOR USE IN THE MANUFACTURE OF LAMINATED GLASS. U. S. 1,762,722. June 10, 1930. George W. Kretzschmar, Garfield, N. J., assignor to Triplex Safety Glass Company of North America, New York. Filed 8/28/28. The inventor's claim follows: An apparatus for use in preparing the edges of laminated glass for sealing comprising an endless, traveling band cleaner, means to support the band cleaner, a movable supporting table to receive the sheet of laminated glass, a presser mounted on the table to press the glass down on the table, means to actuate the same mounted on the table, and means to move the table and the presser toward the band cleaner.

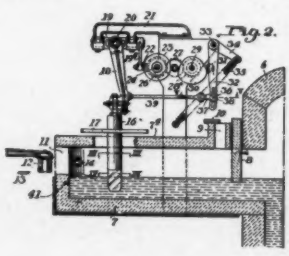
GLASS-CUTTING DEVICE. U. S. 1,762,575. June 10, 1930. Ival G. Fowler, Toledo, O., assignor to The Edward Ford Plate Glass Company, Rossford, O. Filed 7/20/27.

APPARATUS AND METHOD FOR MAKING WIRE GLASS. U. S. 1,791,260. Feb. 3, 1931. George Aurien, St. Louis, Mo., assignor to Mississippi Glass Company, N. Y. Filed 5/7/29. In a machine for forming wire glass, in combination, a pair of rolls forming a pass therebetween for forming a first half-sheet, means comprising one of said rolls for conducting said half-sheet from said pass, whereby said half-sheet is slightly stiffened, means for placing wire mesh on the convex surface of said stiffened half-sheet, and means comprising rolls forming a second roll pass for forming the finished sheet by adding another half-sheet outside of said wire, and means comprising a concave apron for subsequently guiding said sheet to the lehr, said guiding means acting to maintain the wire on the convex surface of the first half-sheet until the sheet is sufficiently stiffened to prevent displacement of the wire from its central position in the sheet.



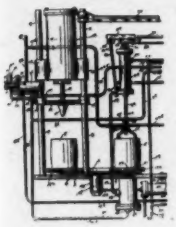
GLASS-FEEDING APPARATUS. U. S. 1,792,932. Feb. 17, 1931. John F. Rule, Toledo, O., assignor to Owens-Illinois Glass Company, Toledo, O. Filed 10/17/27. Apparatus for delivering charges of molten glass comprising a container for the glass having a bottom outlet, a plurality of implements, means for bringing them in succession into operative position over the outlet, and motors individual to said implements and operable to actuate each said implement when in said position to regulate the discharge of a charge of glass.

METHOD OF AND APPARATUS FOR FEEDING MOLTEN GLASS. U. S. 1,791,634. Feb. 10, 1931. Karl E. Peiler, West Hartford, Conn., assignor Hartford-Empire Co., Hartford, Conn. Filed 6/10/26. The method of feeding molten glass, which comprises withdrawing charges of glass from a pool and effecting circulatory movement of the glass in the pool by a member having an orbital movement in contact with the glass along a horizontally disposed endless path located adjacent to the point of withdrawal.



GLASS-SPREADING ROLL. U. S. 1,790,700. Feb. 3, 1931. Paul Joseph Maximilien Escole, Jeumont, France, Assignor to Societe Anonyme des Ateliers de Construction & Fonderies de Jeumont (Anciens Etablissements Th. Haut). Filed 4/21/27.

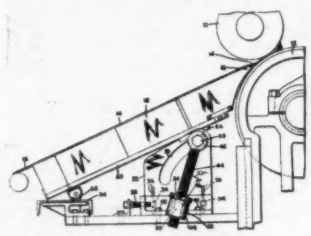
GLASS MACHINE. U. S. 1,792,267. Feb. 10, 1931. Charles Badger, Columbus, O., assignor to Lynch Glass Machine Co., Anderson, Ind. Filed 10/7/15. Machines equipped with the inventor's improvement require only that the gather be placed in the molds in any desired manner, the remaining operations then taking place automatically.



One of the important features of the invention resides in the use of blank molds and blow molds, together with means for automatically transferring the formed blanks. In making some kinds of ware it has been found desirable to use one piece or non-sectional molds in which to form the blanks, and the inventor, therefore, provided a structure for causing a relative movement of the blank out of the blank mold a distance sufficient to enable them to be gripped by means independent of the molds, but this invention is not to be restricted to the use of this type of molds. After the blanks have been gripped or disengaged from the blank molds, means come into play for automatically removing them from the blank mold position and transferring them to the blow molds.

DRAW TABLE AND DRIVE THEREFOR. U. S. 1,793,783. Feb. 24, 1931. John L. Drake and Edwin A. Rosin, Toledo, O., assignors to Libbey-Owens-Ford Glass Company, Toledo, O. Filed 6/10/25. A metallic link for an endless belt glass supporting table having a body portion consisting of spaced top and bottom walls, a web connecting said walls, curved end walls connecting the top and bottom walls, ears projecting longitudinally from the end walls of less width than the top wall, each provided with a transverse opening, the distribution of the metal in at least the top and bottom walls being such as to minimize any tendency toward warping in the presence of glass working temperatures.

APRON CONTROL OF GLASS MACHINES. U. S. 1,791,263. Feb. 3, 1931. Myron L. Begeman and Paul F. Gutmann, St. Louis, Mo., assignors to Mississippi Glass Co., N. Y. Filed 5/21/29. In the manufacture of sheet glass by the continuous process, the newly formed plastic sheet, after leaving the forming rolls, passes over an apron en route to the lehr. After being formed the sheet rests on the lower roll for a certain predetermined arc of rotation and then encounters the nose of the apron, which guides the sheet onto the apron. The object of this invention is to provide devices whereby the position of the apron nose may be adjusted by a single simple operation, and without changing the distance or gap between roll and apron nose.



GLASS-GATHERING APPARATUS AND METHOD. U. S. 1,179,206. Mar. 17, 1931. George E. Howard, Butler, Pa., assignor to Hartford-Empire Company, Hartford, Conn. Filed 7/16/17. In apparatus of the class described, the combination of a container for molten glass having an outlet for discharging the glass in successive suspended masses, and fluid-pressure means located entirely above the outlet for supporting a connected portion of the glass while permitting the discharge of glass from said container, said connected portion forming part of the next succeeding mass.

APPARATUS FOR AND METHOD OF FEEDING MOLTEN GLASS. U. S. 1,796,929. Mar. 17, 1931. George E. Howard, Butler, Pa., assignor to Hartford-Empire Company, Hartford, Conn. Filed 6/9/23.

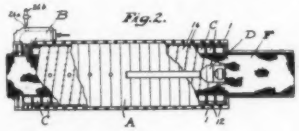
APPARATUS FOR DRAWING SHEET GLASS. U. S. 1,795,943. Mar. 10, 1931. Wert French, Charleston, W. Va., assignor to Libbey-Owens-Ford Glass Company, Toledo, O. Filed 2/7/27. Hollow metallic, internally cooled members arranged transversely of and at opposite sides of the sheet for cooling the glass just prior to its introduction into the sheet.

TREATING GLASS ARTICLES. U. S. 1,791,066. Feb. 3, 1931. Rowland D. Smith, Corning, N. Y., assignor to Corning Glass Works, Corning, N. Y. Filed 4/30/30. The method of treating frosted glass articles which includes washing them in a water solution of a simple aluminum salt of an aliphatic organic acid.

GLASS-SHEET DRAWING APPARATUS. U. S. 1,795,254. Mar. 3, 1931. Paul Escole, Jeumont, France, assignor to Ateliers de Construction & Fonderies de Jeumont (Anciens Etablissements Th. Haut). Filed 3/19/30. In glass sheet drawing apparatus, including a pair of relatively movable rollers and means for pressing said rollers against opposite faces of the sheet, a suspension device for the movable roller, comprising a lever, a fixed pivot, a knife edge resting upon said pivot and by which said lever is carried, a bearing bush for the trunnion of said roller, said bush being mounted in said lever and flexibly carried from said pivot, a pair of intermeshing gears at fixed centers, and flexible driving connections between the trunnions of said rollers and said intermeshing gears.

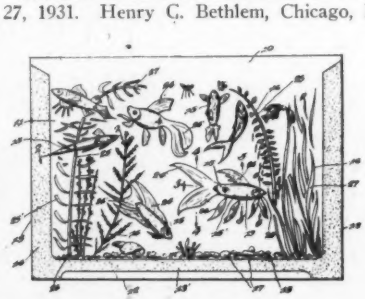
MACHINE FOR FORMING HOLLOW GLASS ARTICLES. U. S. 1,789,471. Jan. 30, 1931. Byrne McGovern, Evansville, Ind., assignor to Owens-Illinois Glass Company, Toledo, O. Filed 6/4/28. A mold bottom plate formed with passageways extending upwardly therethrough for the passage of cooling air and opening laterally to the exterior of the bottom plate at a position or positions below the upper surface of said plate, a hollow plate holder on which said plate is mounted, said plate holder being provided with passageways for the passage of cooling air through the upper wall of the plate holder.

GLASS-ANNEALING LEHR. U. S. 1,790,630. Jan. 27, 1931. Karl E. Peiler, West Hartford, Conn., assignor to Hartford-Empire Company, Hartford, Conn. Filed 1/9/30. An object of the invention is to supply heat to the space which is located between the inclined portion of the foremost turn of the helical flue and the right angular end of the lehr and which is not included within the helical flue. A further object is to design the flue-forming members of a substantially helical flue lehr, so as to render them simple to construct and assemble, and more specifically, so that in the construction of these members, no cores are required for the castings, and the machining necessary is of the simplest kind. Also it is an object to design these flue-forming members in such a way that certain of the flue sections of each turn are at right angles to the direction of movement of the glass through the lehr, while others are arranged diagonally thereof to connect opposite ends of contiguous right angular portions to form a continuous flue.



METHOD AND APPARATUS FOR FEEDING MOLTEN GLASS. U. S. 1,789,480. Jan. 20, 1931. Leonard D. Soubier, Toledo, O., assignor to Owens-Illinois Glass Company, Toledo, O. Filed 8/22/27. In combination, a container for molten glass having a bottom outlet orifice, a cup arranged to periodically enclose the lower side of said orifice, said cup comprising a pair of telescoped sections, means to normally hold said sections in their extended positions, means to cause a relative movement of said sections while the cup encloses said outlet orifice to create super-atmospheric pressure internally of the cup causing upward movement of glass in said orifice, and means operating at predetermined time intervals to apply vacuum internally of the cup to accelerate outward flow of glass through said orifice.

METHOD OF MAKING PICTORIAL GLASSES. U. S. 1,790,531. Jan. 27, 1931. Henry C. Bethlem, Chicago, Ill. Filed 6/12/29. The method of making an artificial aquarium from a glass body consisting in rough grinding the edge portions of the body to cause said edge portions to present the appearance of a frame around the aquarium and applying colored characters in the enclosed portion thereof.



Ceramics Exposition at Rutgers University Well Attended

E. C. BOOZ' BOTTLE

A most successful Ceramics Exposition has just been brought to a close at Rutgers University, New Brunswick, N. J. The Exposition, which was sponsored by the Rutgers Ceramic Club, a student organization, ran from March 17 to 21, inclusive.

Many interesting exhibits, ranging from early New Jersey pottery and glass to the most modern products of ceramic manufacturers in the State were on display.

The early New Jersey pottery and glass was displayed through the courtesy of the owners, Mr. and Mrs. Hugh Williamson Kelly of Woodbridge, N. J.

The "Wistarberg" bowl had a particular appeal for visitors to the Exposition. Wistarberg ware was made by Caspar Wistar and his associates near Allowaystown, Salem County, during the period 1738-1770. Wistar sent to Europe for expert glass blowers and successfully engaged in the business until 1770, when he had to give up on account of the desertion of his laborers, who were determined to become land owners and engage in farming.

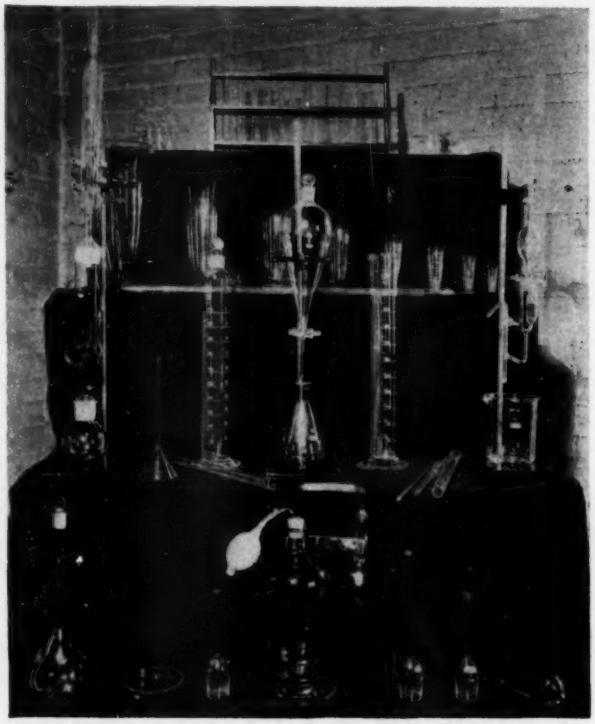
Light glass pitchers and vases with lily pad decoration, all of early South Jersey manufacture, were included in the exhibit. While sometimes showing uneven molding and cloudy effects, even the simple household utensils of the early colonials have a rugged beauty. Other pitchers and vases in rich deep blue added a note of color to the exhibit.

A blown glass tumbler inscribed "WELCOME LAFAYETTE" was one of the most interesting features of the exhibit. This tumbler was made in honor of Lafayette on the occasion of a banquet tendered him by General Gates at York, Pennsylvania.

Bottles of distinction were included in the group. An amber "Booz" bottle, made by Whitney Bros. at Woodbury, New Jersey, about 1870 attracted considerable attention. Bottles of this type were designed to contain "E. C. Booz's Log Cabin Whiskey" and the bottle itself, as shown, is of the log cabin shape. It is easy to understand how the name "Booz" came to be applied to the popular drink of that time, and has continued through these many years.

Other interesting glass bottles in this exhibit were the "Baltimore Monument" bottle, claret colored, and bearing an imprint of the Monument to which it was dedicated; also a dark blue calabash bottle with imprint of Washington on one side and a tree on the other.

After leaving the exhibit of early New Jersey wares, the visitors to the Exposition had an opportunity to view glass wares in the modern trend as exemplified by the display of Edmondson Warrin, Inc., of Upper Montclair, N. J., and New York City. A particularly interesting piece was the bottle of rich deep blue overlaid with silver. Other beautifully decorated glass wares, some with monogram to match the china displayed, were of more than passing interest to the visitors.



SCIENTIFIC GLASSWARE BY KIMBLE GLASS COMPANY

EARLY NEW JERSEY GLASS AND POTTERY AT RUTGERS' UNIVERSITY EXHIBITION

Scientific glassware from the Kimble Glass Company, Vineland, was grouped in impressive array in the chemistry laboratory of the Ceramics Building. This included biological, chemical and metallurgical glassware specialties of intricate shape and design.

The Salem Glass Company of Salem exhibited a line of bottles of all kinds. Attractive color effects, unusual shapes and sizes were shown in the bottles manufactured by this company.

The General Electric Company submitted a most interesting exhibit of fused quartz products. This included lenses for optical purposes, special chemical apparatus, rods for high temperature work, window panes, etc.

The products of more than sixty ceramic manufacturers in New Jersey were also on display at the Exposition. These included terra cotta, brick of all kinds, fireproofing, refractory products, hollow tile, floor and wall tile, sanitary ware, hotel china, belleek china, art pottery, ceramic materials, ceramic machinery, etc.

A glass blower greatly added to the interest of the Exposition. His booth in the machinery room of the Ceramics Building was one of the centers of attraction.

More than four thousand people visited the Exposition and were impressed with the wide variety and high quality of ceramic products manufactured in New Jersey.

This exposition is the second venture of its kind by the Rutgers Ceramics Club. All of the work was done under the supervision of Professor George H. Brown, Director of the Department of Ceramics, assisted by his staff and students.

The Glass World and What It Is Doing

News of the Industry

General Electric Promotions

J. W. Kewley, until recently acting manager of the General Electric Company's incandescent lamp department, Cleveland, was recently promoted to be manager of the department T. W. Frech, who was given a year's leave of absence as manager of the lamp department to head the R. C. A. Radiotron Company at Harrison, New Jersey, has now been given an additional year's leave.

J. W. KEWLEY

At a meeting of the Directors of the General Electric Company a short time ago, it was announced by President Swope that T. K. Quinn of Cleveland and Charles E. Wilson of Bridgeport, Conn., were elected vice-presidents of the company. H. H. Barnes, Jr. in charge of the New York district was made a commercial vice-president, J. L. Buchannan was named president of the General Electric Supply Corporation, affiliated with General Electric Co., and operating a bulb frosting plant at Pittsburgh.

Tariff Investigations Ordered

The United States Tariff Commission on March 24 regarding an investigation under section 336 of the Tariff Act of 1930 of the differences in cost of production of, and of all other facts and conditions enumerated in said section, with reference to gauge glass tubes, ordered a public hearing held at a time and place to be fixed later by the Commission.

The Commission on February 21, 1930 has also announced another investigation, No. 53, on non-edible gelatin and glue, to be held at a time and place to be announced later.

Another investigation under section 332 (g) of the Tariff Act of 1930 for the purpose of ascertaining the differences in the cost of production of crude petroleum, fuel oil, gasoline and lubricating oils in the United States and foreign countries. The results of this investigation will be reported to the president and to the House of Representatives not later than the beginning of the next regular session of Congress.

In addition to the investigation No. 35 on blown glass tableware and kitchen ware which was recently postponed until May 14, 1931, and No. 20 on window glass recently postponed until May 15, 1931, the Commission also has ordered investigation No. 30 on laminated products of which a synthetic resin or a resin-like substance is the chief binding agent in sheets or plates [such as laminated safety glass.]

The Imperial Glass Company, Bellaire, Ohio on February 28 at the request of creditors was put into the hands of J. M. Dubois. Temporary arrangements were made, however, to continue the plant in operation.

Progress of Laminated Glass

According to a report from Paris the invention of laminated safety glass was the result of an accident in the laboratory of Edouard Benedictus, a French poet-chemist. Rummaging around his laboratory, Benedictus, the report says, accidentally knocked down a test tube. It fell to the floor but failed to break. On investigation it was found that while the glass had cracked into many pieces, each piece was held to the next by a dried up mixture which had been in the tube for years. He analyzed the mixture and found it to be alcohol, ether, acetone, amyl acetate and trinitrocellulose. Utilizing the facts he had discovered Benedictus developed the invention of safety glass. There is little doubt that this type of glass will supersede all others for use in vehicles of all types for public and private service. In a number of the United States laws have already been passed making its use compulsory in all public conveyances.

Many automobile manufacturers are equipping part or all of their models with windshields and in some cases completely with safety glass. According to the Triplex Safety Glass Company, Massachusetts last year passed a bill requiring non-shatterable glass on public carriages. New York State introduced a similar bill at Albany and in the City of New York a police ordinance specifying the glass to be used in taxis is in force.

In Canada steps are being taken to enact similar laws. Recently the English Parliament through the Ministry of Transport put in force a road act to the effect that all new vehicles put on the market after January 1, 1932, must be completely equipped while cars now in use, it is reported, are exempt until January 1, 1937.

The French Department of Commerce has recently recommended that the 20,000 taxis in Paris be equipped with safety glass. The French government reported 67% of auto injuries as due to broken glass. This is slightly higher than the American records show.

In January and February of 1931 action was taken to obtain similar protective legislation in Minnesota, Pennsylvania, Delaware, Connecticut, Rhode Island, Ohio, New Jersey and Michigan.

Hazel-Atlas Glass Company at its annual meeting late in February re-elected its officers as follows: J. C. Brady, chairman of the board of directors; J. H. McNash, president; C. R. Hubbard, A. F. Brady, and Walter McClure, vice-presidents, with Mr. McClure also in charge of sales. G. S. Quay was re-elected secretary, B. Harrison Bruhn, assistant treasurer, and J. S. Algeo, sales manager.

The American Plate Glass Company's bond holders protective committee recently discussed a a meeting of the board of directors of the Chamber of Commerce, Kane, Pa., new plans for re-financing the Company. It was decided that a loan of $200,000, to be raised from local residents, would be required to which the bond holders committee would add $100,000, the entire sum $300,000 to be used only as working capital.

Eureka Tumbler Company's long idle plant at Cameron, W. Va., according to a report from Wheeling, Va. has changed hands. Akron, Ohio interests are said to be taking over the plant with the intention of starting operation within a few weeks.

Fifty Years of Usefulness in the Glass Industry.

Fifty years of service in the glass industry, a term of service notable both for its length and for the fact that the entire period has been spent with one concern, is the record of George S. Bacon, vice-president and general manager of Whitall Tatum Company, Millville, N. J.

On March 21, 1931 Mr. Bacon rounded out his first half century in the glass field. He entered the employ of the Whitall Tatum Company on March 21, 1881 as office boy in their Philadelphia office located at 410 Race Street. He remained in Philadelphia

GEORGE S. BACON

until December 12, 1881, when he was sent to the factory at Millville as a sort of combination office boy and assistant to the cashier. He progressed through various departments of the factory until July 1, 1897 when he became manager of the Green Works, succeeding Mr. John Mickle. On July 1, 1897 he became manager of the Flint Works, succeeding Mr. Bond Thomas. From this latter date he has been general manager of both plants of the company, a member of the Board of Directors since July 26, 1910, and a vice-president since October 27, 1926.

His thirty-three years of service as general manager of Whitall Tatum Company, establish a record for this company, the longest previous service as manager being twenty-three years.

During the fifty years that he has been connected with Whitall Tatum Company, he has seen glass made by every method used up to the present time, namely—open pots, covered pots, day tanks and continuous tanks. Under his direction, Whitall Tatum Company became the first glass company to make flint glass in a day tank furnace. This was in 1895, and the tank was built at the Green Works as an experiment. In 1897, he was instrumental in bringing about the construction of the first continuous tank furnace for the making of flint glass. So far as the Company is able to determine Whitall Tatum Company operated the first day tank and the first continuous tank for flint glass, and Mr. Bacon's was the guiding hand in the construction and operation of both types.

He has also seen bottles made by every known method—by hand (including off-hand, clay mold, wooden mold, paste mold and iron mold), semi-automatic machine, automatic machine (both the vacuum and feeder methods), and has seen the evolution of annealing develop from the days of ovens, through open-fired narrow lehrs, muffle lehrs and the present unit lehrs.

During his fifty years in the industry, he has visited practically every glass factory in the United States and Canada.

He served continuously as a member of the Wage Committee of the National Bottle Manufacturers' Association from 1895 to 1925, and has been a director of the Glass Container Association since its beginning. He was also a director of the National Bottle Manufacturers' Association from 1895 until it was merged with the Glass Container Association. During his connection with the National Bottle Manufacturers' Association Mr. Bacon also served as vice-president, chairman of the managing committee and as secretary.

He was a director of the West Jersey & Seashore Division of the Pennsylvania Railroad, a Director of the Millville National Bank, and a member of Old Colony Club, the Union League of Philadelphia and the Manufacturers' Club of Philadelphia.

February Plate Glass Production

The compilation prepared by P. A. Hughes, secretary of Plate Glass Manufacturers' Association, issued March 18, 1931, shows the production of polished plate glass in the United States for the month of February, 1931, to have been 8,881,520 sq. ft., as compared to 7,320,675 sq. ft. produced in the preceding month, January, 1931, and 9,804,464 sq. ft. produced in the corresponding month last year, February, 1930.

In **"The Influence of Various Radiations on the Coloration of Glass"**, P. Gilard (in *Chimie et Industrie*, vol. 24, pp. 1035-1051) included a glass corresponding to the composition 6 SiO_2, CaO, K_2O, decolorized by nickel oxide.

E. W. TILLOTSON
Mellon Institute
Pittsburgh, Pa.

Celebrities at Cleveland

These two pictures by E. L. Hettinger of Willson Products, Inc., Reading, Pa., show some of the Glass Division luminaries outside the Cleveland Auditorium, at the annual meeting in February.

Dr. Cohn's presence was a very welcome feature of the meeting, and his paper on the blue glow of thorium under cathode ray bombardment one of the most interesting of the session.

ALEXANDER SILVERMAN
University of Pittsburgh

DR. WILLI COHN
Berlin

Columbus Plant Working Night Shift

Miller Machine & Mold Works, manufacturers of glass house machinery, 705-719 Ann Street, Columbus, Ohio, are working 22 hours out of every 24. The company is extremely busy and each month's output is exceeding the preceding month. Andrew G. Doll, secretary and treasurer, states their export business also is very good. Summing up the conditions in general the outlook is very encouraging and if there is a continuation of present conditions, the Miller company expects to exceed their sales of 1930 which was their banner year.

Recent Deaths

William A. Hamann

A career of almost half a century in the chemical manufacturing industry was brought to a close with the recent retirement of William A. Hamann, as chairman and director of the Roessler & Hasslacher Chemical Co., Inc., New York, N. Y. Retirement was due to a desire to give up active business. The company operates plants at Niagara Falls, N. Y.; Perth Amboy, N. J. and El Monte, Calif., producing a variety of chemical specialties which are used in many industries.

It was in 1885 that Mr. Hamann joined Roessler and Hasslacher, as the present company was then known.

As the company grew, Mr. Hamann gradually assumed greater responsibilities. He was successively secretary, treasurer, vice president, and in 1926, president of the company. In the early part of 1928, Mr. Hamann became chairman of the board.

Mr. Hamann's long service with the company was marked by the continuous and sturdy growth of the concern to one of the leading chemical manufacturers in the United States.

Mr. Hamann has not given out his plans, other than travel and a more active interest in Elka Park, a cooperative summer home enterprise, located in the Catskills, of which he has been treasurer for a good many years.

Alfred Bishton Botfield

Alfred Bishton Botfield, originator of high temperature cement and founder of that industry in the United States, died recently in Miami, Florida, at the age of 83. He was born September 20th, 1847 at Shifnal, Shropshire, England, and received his education in schools and universities of that country.

Later he established the Botfield Furnace Specialties Company in Philadelphia engaging in the building and repairing of stationary and marine boiler settings. He soon recognized the deficiencies of mortars then in vogue for laying up fire brick and began his earliest experiments to develop a mortar which would function as a cement, to bond brick to brick.

In 1907, Mr. Botfield produced the first commercial batch of his new bonding material, terming it Adamant, and it was used for the bonding of fire brick in boiler settings at the Continental Dye Works in Philadelphia.

Commercial acceptance of his new high temperature bonding material progressed slowly for a number of years, but his original batch of a few hundred pounds of high temperature cement was the forerunner of the many thousands of tons of high temperature refractory cement that are produced annually in the United States at the present time.

In 1915, Mr. Botfield retired from active business, and the conduct of the Botfield Furnace Specialties Company was assumed by his son, Leonard Bishton Botfield who is now President of the succeeding Philadelphia concern with the corporate title of Botfield Refractories Company.

Thomas R. Evans

Thomas Raymond Evans, president of the Diamond Alkali Company, died March 17 in his home on Beechwood Boulevard, Pittsburgh, Pa. He was about 52 years of age having been born in 1878, the son of Thomas Evans and Henryetta Sallisbury Evans. His father, Thomas Evans was one of the earliest of the glass manufacturers who located in Pittsburgh. When the Macbeth-Evans Glass Company was organized Thomas Raymond Evans joined them as a purchasing agent. In 1910 he helped to organize the Diamond Alkali Company of which he became assistant treasurer and later he filled the offices of general manager, treasurer, director and vice-president, then in 1921 became president. He was a member of the American Chemical Society and the Engineering Society of Western Pennsylvania. He was a member of several city and country clubs.

Besides his widow, Mrs. Ida Flaccus Evans, three daughters, two sons and one brother survive him.

William Weber.

William Weber, for many years connected with the glass manufacturing industry and a director at times of three different companies, died in Weston, W. Va. early in March.

Inquiries Received

For further information address THE GLASS INDUSTRY

538. We are desirous of locating a glass factory to make a large quantity of Chemical or Bunsen funnels for us. We have the molds for making these funnels, and would appreciate information as to a probable source of production.

539. We are interested in obtaining two six-inch diameter plate glass disks.

540. We are anxious to get the names of glass manufacturers who make glass reflectors, used as danger signs on highways, automobile tail lights, etc.

541. Are there any firms in the United States manufacturing small three minute sand glasses like those used in timing eggs? I will require quite a few thousand.

542. Please refer me to a source of supply for paste that can be applied on glass, burned in, for marking purposes.

What the World Wants

Specific Inquiries for American Goods Received in the Department of Commerce, Washington, D. C. For further information write the department.

Canada—50658, Glass, electric fixtures.
Canada—50601, Lamps, health, electric.
Santo Domingo—50635, Glass flasks, 27 and 52 ounces.
Colombia—50566, Glass tubes and precision glass faucets.
Peru—50552, Glassware, laboratory.
Canada—50537, Glassware, office, such as sponge cups, ash trays, and moisteners.
Italy—50584, Glassware, pressed, in distinctive fancy designs.

Readers Wants and Offers

Address answers to all "keyed" ads c/o The GLASS INDUSTRY 24 West 40th St., New York

SITUATION WANTED ABROAD OR OVERSEAS

Engineer, first-rate glass works expert, efficient in every kind of glass technical work, glass melting, making of pots and stones, construction of furnaces, pot and tank furnaces, worked by hand or by machinery, desires situation. Competent to modernize and reconstruct old-fashioned glass works or to fit up new works perfectly up-to-date in the manufacture of bottle, lighting, plate, window, optic, crystal and colored glass as well as glass refining.

Offers to W. Hermanck, Schnurpfeil's Review for Glass-Works, München, Germany, Elisabethstr. 48.

SITUATION WANTED

By Glass Technologist and Engineer, as factory manager now employed. Many years experience on both plain and colored glass, tanks and pot furnaces. Would like to get in touch with some progressive company who wants to do things. Address "Class A3" as above.

EXPERIENCED TUMBLER DECORATOR

Wanted: Man with experience in decoration of tumblers with letters and names to be used for advertising purposes. Address "Classified F1."

BACK NUMBERS WANTED

Will pay moderate premium for copies in good condition of THE GLASS INDUSTRY, Vol. 9, December, 1928, and Vol. 11, December, 1930. Address THE GLASS INDUSTRY, as above.

Current Prices of Glass-Making Materials

March 23, 1931

Quotations furnished by various producers, manufacturers and dealers

		Carlots	Less Carlots
Acid			
Citric (dom.)	lb.	.40	46
Hydrochloric (HCl) 20° tanks, per 100 lb		..	1.10
Hydrofluoric (HF) 60% (lead carboy)	lb.	..	.13½
52% and 48%	lb.	.10	.10-.11½
Nitric (HNO_3) 38° carboy ext. Per 100 lb.		5.50	..
Sulphuric (H_2SO_4) 66° tank cars	ton	15.50	..
Tartaric	lb.	..	.31½
Alconol, denatured	gal.	..	.32
Aluminum hydrate ($Al(OH)_3$)	lb.	.04½-.05	.05½-.06
Aluminum oxide (Al_2O_3)	lb.	..	.07
Ammonium bifluoride (NH_4) FHF	lb.	..	.19
Ammonia water (NH_4OH) 26° drums	lb.	.02½	.02¾
Antimony, metallic (Sb)	lb.	..	.09⅝
Antimony oxide (Sb_2O_3)	lb.	..	.09⅝
Antimony sulphide (Sb_2S_3)	lb.	..	.14
Arsenic trioxide (As_2O_3) (dense white), 99%	lb.	.04	.04½
Barium carbonate ($BaCO_3$), Crude, (Witherite) 90%, 99% through 200 mesh	ton	47.00	..
90% through 100 mesh	ton	44.00	..
Barium hydrate ($Ba(OH)_2$)	lb.	..	.05-.05½
Barium mixture, glassmaker's, f.o.b. St. Louis	ton	25.00	..
Barium nitrate ($Ba(NO_3)_2$)	lb.	.08	.08¼
Barium selenite ($BaSeO_3$)	lb.	..	..
Barium sulphate, in bags	ton	19.00	24.00
Barium sulphate, glassmaker's, carlots, bulk, f.o.b. shipping point,	ton	15.00-16.00	18.00
Bone ash	carlots, lb.	.06	.06½
Borax ($Na_2B_4O_7 10H_2O$)	lb.	..	.0355-.0425
Crystal	lb.	.028-.033	..
Granulated	lb.	.025-.03	..
Powdered	lb.	.02875-.03375	..
Boric acid (H_3BO_3)	lb.	.0625-.07125	.0625-.08125
Refined	lb.	.0625-.07125	.07125-.08125
Cadmium sulphide (CdS)—			
Red	lb.	..	.65-.90
Orange	lb.	..	.65-.90
Yellow	lb.	..	1.30-1.50
Chromium oxide (Cr_2O_3)	lb.	.24	.26
Cobalt oxide (Co_2O_3)			
In bbls.	lb.	..	1.75-1.85
In 10 lb. tins	lb.	..	1.85
Copper oxide			
Red (Cu_2O)	lb.	..	.25
Black (CuO)	lb.	..	.18-.25
Black prepared	lb.	..	.22
Cryolite ($Na_3Al F_6$) Natural Greenland			
Kryolith)	lb.	.09	.10-.10½
Synthetic (Artificial)	lb.	..	.09½
Epsom salts ($MgSO_4$) (imported) Per 100 lb.		..	1.15-1.20
Feldspar—			
100 mesh	ton	12.00-18.00	13.50-20.00
80 mesh	ton	11.00-11.75	14.50
40 mesh	ton	11.00	13.50
20 mesh	ton	10.00	10.50
Fluorspar (CaF_2) domestic, ground, 95-98% (max SiO_2, 2½%)			
Bulk, carloads, f.o.b. mines	ton	32.50	..
In bags or barrels	ton	36.50	41.50
Imported	ton	36.50	38.50-40.00
Formaldehyde	lb.	..	.07½-.07¾
Graphite (C)	lb	..	.04-.07
Iron oxide—			
Red (Fe_2O_3)	lb	..	.0450
Black (FeO)	lb	.04½	..
Kaolin (f.o.b. mine)	ton	8.00-9.00	..
English, lump, f.o.b. New York	ton	14.50-25.00	24.50-30.00
Kryolith (see Cryolite)		Carlots	Less Carlots
Lead chromate ($PbCrO_4$)	lb.	..	30
Lead oxide (Pb_3O_4) (red lead)	lb.	.07	.08
Litharge (PbO)	lb.	.06	.07
Lime—			
Hydrated ($Ca(OH)_2$) (in paper sacks)	ton	7.75	..
Burnt (CaO) ground, in bulk	ton	6.00	..
Burnt, ground, in paper sacks	ton	8.00	..
Burnt, ground, in 280 lb. bbls.	Per bbl.	2.15	2.30
Limestone ($CaCO_3$)		1.75-2.50	..
Magnesia (MgO)—			
Calcined, heavy (in bbls.)	lb.	.06	.07
light (in bbls.)	lb.	..	.23
extra light (in bbls.)	lb.	..	.37
Magnesium carbonate ($MgCO_3$)	lb.	.06	.07-.10½
Manganese 85% (MnO_2)	lb.	.03	.03
Nickel oxide (Ni_2O_3), black— for nickel content	lb.	..	.35
Nickel monoxide (NiO), green— for nickel content	lb.	..	.35
Plaster of Paris, bags	ton	21.00	23.00-29.00
Potassium bichromate ($K_2Cr_2O_7$)—			
Crystals	lb.	.09	.09¼
Ground	lb.	11	.12
Potassium carbonate—94-96%	lb.	.0555	.0555
Calcined (K_2CO_3) 96-98%	lb.	.06½	.07¼
Hydrated 80-85%	lb.	.05¾	.06¼
Potassium chromate (K_2CrO_4)	lb.	..	.23-.32
Potassium hydrate (KOH) (caustic potash)	lb.	.07⅛	.08
Potassium nitrate (KNO_3) (gran.)	lb.	..	.06½-.06¾
Potassium permanganate ($KMnO_4$)	lb.	.16	.17
Powdered blue	lb.	..	.22
Rochelle salts, bbls.	lb.	..	.19
Rouge	lb.	..	..
Rutile (TiO_2) powdered, 95%	lb.	.15-.20	.20-.25
Salt cake, glassmakers (Na_2SO_4)	ton	22.00	..
Selenium (Se)	lb	..	1.80
Silver nitrate ($AgNO_3$)	(100 oz.) per oz.	..	.23
Soda ash (Na_2CO_3) dense, 58%—			
Bulk, on contract	Flat per 100 lb.	1.07½	..
In barrels	Per 100 lb.	1.38	1.90-2.00
In bags	Per 100 lb.	1.17½	1.72½
Spot orders.. .025 per 100 lbs. higher		..	..
Sodium bichromate ($Na_2Cr_2O_7$)	lb	.07	.07½
Sodium hydrate (NaOH) (caustic soda) Solid	Per 100 lb.	2.50	..
Sodium nitrate ($NaNO_3$)—			
Refined (gran.) in bbls.	lb.	.03¾	.04½
95 per cent.	Per 100 lb.	2.01½-2.08	2.15-2.25
Sodium selenite (Na_2SeO_3)	lb	..	2.00
Sodium fluosilicate (Na_2SiF_6)	lb	.05	.05½
Sodium uranate (Na_2UO_4) Yellow or Orange	lb.	..	1.50-1.55
Sulphur (S)—			
Flowers, in bbls.	Per 100 lb	3.45	3.80-4.00
Flowers, in bags	Per 100 lb	3.10	3.45-3.65
Flour, heavy in bbls.	Per 100 lb.	2.85	3.20-3.40
Tin chloride ($SnCl_2$) (crystals)	lb.	.37½	.39
Tin oxide (SnO_2) in bbls.	lb.	.28	.30-.35
Uranium oxide (UO_2) (black, 96% U_3O_8)			
100 lb. lots. Black	lb.	..	2.75
Yellow	lb.	..	1.50
Zinc oxide (ZnO)	lb.	.08½	.12
American process, Bags	lb.	.06½	.07
Zircon			
Granular (Milled .005-.02c higher)		.07	.07½-.08
Crude, Gran. (Milled .005-.02c higher)		03¼	.04-.05

Monthly Summary of United States Foreign Commerce in Glass

EXPORTS

Corrected to February 24, 1931.

	January 1930 Quantity	January 1930 Value	January 1931 Quantity	January 1931 Value	Six Months Ending December 1929 Quantity	Six Months Ending December 1929 Value	Six Months Ending December 1930 Quantity	Six Months Ending December 1930 Value
Glass and glass products (Total)	.....	$789,352	.....	$647,515	.....	$5,432,762	.....	$4,237,024
Plate and window glass—								
Window glass, common, box 50 sq. ft.	2,896	15,708	813	4,375	4,847	33,135	5,383	29,567
Plate glass, unsilvered, sq. ft.	178,334	65,551	374,036	106,224	888,452	340,584	1,570,801	494,660
Other window and plate glass lbs.	373,192	28,125	405,327	32,543	2,513,631	272,239	2,576,375	194,368
Glass containers (bottles, vials and jars)	.....	246,147	.....	210,155	.....	1,830,981	.....	1,485,754
Table glassware, plain	.....	120,321	.....	67,906	.....	759,771	.....	459,642
Table and other glassware, cut or engraved	.....	8,192	.....	3,449	.....	73,737	.....	47,087
Lamp chimneys and lantern globes lbs.	.....	16,460	.....	13,324	.....	159,046	.....	96,328
Globes and shades for lighting fixtures lbs.	.....	52,151	.....	45,219	.....	364,137	.....	253,502
Chemical glassware lbs.	23,089	22,279	14,786	15,225	171,171	141,198	148,960	118,200
Electrical glassware, except for lighting lbs.	514,938	37,628	106,047	10,764	1,405,896	141,467	781,838	65,434
Other glassware	.....	176,790	.....	138,331	.....	1,316,467	.....	992,482

IMPORTS

Corrected to February 24, 1931.

Glass and glass products	.....	$861,918	.....	$495,229	.....	$7,287,051	.....	$4,256,843
Cylinder, crown, and sheet—								
Plain dut. lb.	2,930,139	114,469	777,960	32,720	22,843,684	788,312	3,857,393	148,934
Bent, beveled, colored, etc. dut. lb.	.....	43,947	137,702	20,506	.....	234,388	1,396,417	146,147
Plate glass dut. sq. ft.	690,825	146,957	390,931	100,384	6,737,129	1,340,896	2,687,111	572,388
Glass mirrors	.....	.....	188	383	.....	.....	427	1,048
Rolled, cylinder, crown, and sheet glass, ground, obscured, bent, beveled, colored, etc.	.....	.....	.....	4,182	.....	.....	.....	26,734
Laminated glass and manufactures, and plated glass	.....	.....	.....	944	.....	.....	.....	11,581
Bottles, vials, jars, and other containers	.....	101,788	.....	44,584	.....	184,350	.....	438,994
Scientific articles and utensils dut.	.....	51,026	.....	30,718	.....	351,955	.....	204,288
Tubes and rods dut.	.....	.....	.....	6,620	.....	.....	.....	48,961
Illuminating articles dut.	.....	57,240	.....	40,841	.....	351,064	.....	275,136
Blown glass articles dut.	.....	223,814	.....	.....	.....	3,092,977	.....	1,710,440
Bulbs for electric lamps, without filament dut.	.....	.....	1,479,908	13,440	.....	.....	.....	.....
Other blown glass articles dut.	.....	.....	.....	123,587	.....	.....	.....	.....
Pressed glass articles	.....	16,341	.....	9,604	.....	151,153	.....	122,550
Other glassware	.....	106,336	.....	66,716	.....	791,956	.....	549,342